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# STUDIES ON MODIFICATIONS OF SOLID INDUSTRIAL WASTES

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# STUDIES ON MODIFICATIONS OF SOLID INDUSTRIAL WASTES

By

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From February 1, 1968 to June 30, 1971, Syracuse University conducted a continuing series of "Studies on Modifications of Solid Industrial Wastes." This report consists of papers prepared for the series. Topics included were: collection and analysis of data on solid industrial wastes; physical properties of Solvay industrial waste bed materials; rehabilitation of solid industrial waste disposal sites; rehabilitation of the Solvay process waste beds; modifications of Solvay process solid waste disposal; inhibition of acid mine drainage by municipal solid waste effluents; use of solid industrial wastes in the preparation of construction materials; and effect of humus matter on retention of nitrogen fertilizers in soils.

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# FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to solve the problems involved in solid waste disposal, this report presents a series of papers written to study modifications of solid industrial wastes.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

## Preface

From February 1, 1968 to June 30, 1971 Syracuse University (Syracuse, New York 13210) conducted a continuing series of "Studies on Modifications of Solid Industrial Wastes." During this period it was demonstrated that limited data are available because of limited research on rehabilitation, reclamation and resource recovery of "solid industrial wastes". This is due to the low visibility and to the non-required viability of a very high percentage of total solid wastes. Publicity efforts by mass media (newspapers, journals, radio and television) have been concentrated on the obvious problems of environments, i.e., residential, commercial and institutional solid wastes. Collection problems have limited exposure, although 80% of budgeted dollars go to collection costs; disposal in open dumps, burning dumps and euphemistic sanitary land fills have been publicized by all civic-minded citizens, politicians, organizations and mass media.

It is obvious from the following quotes that the most visible but least important sources of solid wastes come from the identifiable "residential, commercial and institutional wastes": "The total solid wastes produced in the United States in 1969 reached 4.3 billion tons as shown in the following table:

| | |
|---|---|
| Residential, Commercial and Institutional Wastes | 250 (Million tons) |
| Collected | (190) |
| Uncollected | (60) |
| Industrial Wastes | 110 |
| Mineral Wastes | 1,700 |
| Agricultural Wastes | 2,280 |
| Total | 4,340 (Millions of tons) |

Many of these originated from agriculture and livestock. Other large amounts arose from mining and industrial processes. A little under 6 percent, or 250 million tons, were classified as residential, commercial and institutional solid wastes, and only three-fourths of this was collected."

(Note: The complete reference for the quoted table is: *Waste Age*, September-October, 1970. The original source is *Environmental Quality: The First Annual Report of the Council on Environmental Quality* together with *The President's Message* transmitted to Congress in August, 1970. The original source data came from the Bureau of Solid Waste Management, Department of Health, Education and Welfare; and, from the Division of Solid Wastes, Bureau of Mines, Department of Interior.)

It becomes very apparent early to workers in the solid waste collection and disposal fields that 6% of solid wastes demand a much higher and disproportionate percentage of effort in research, development, and demonstration. Uncollected and spilled municipal refuse, open dumps, burning dumps and poorly operated sanitary landfills are highly visible to the general public and to their elected governmental representatives. Thus, emphasis is placed upon 6% of the total problem. What happens to the other 94% of solid wastes?

Data and information in published sources were widely distributed. Many of the source references were in journals of recent, and, frequently of limited and obscure circulation. It was, therefore, recognized early in the series of studies that progress on the overall project plan could be facilitated only by extensive collection and correlation of source material. Such data required, in addition, a requisite emphasis for evaluation of personal interviews with many producers of solid industrial waste (e.g., pharmacutical, chemical and ceramic manufacturers) as well as direct contacts with collectors and disposers of such materials whether municipal, private or industrial operators.

The following list of reports and papers were prepared under the original and continuing grants. Copies were made available to the Bureau of Solid Waste Management in Cincinnati, Ohio, for dissemination through SWIRS (Solid Waste Information Retrieval System) to personnel and facilities which demonstrated cognizant needs. (N.B. The current name and address of the grantor facility are: Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268.)

These are listed in chronological order:

1. *Studies of Modifications of Solid Industrial Wastes* Progress Report, Part I, *Collection and Analysis of Data on Solid Industrial Wastes,* Grant No. 5-R01-U1-00537-01A1, C. S. Grove, Jr., N. L. Nemerow, M. Kestner, and Fred Boecher, December 31, 1968, (Syracuse University, Syracuse, N. Y. 13210).

2. *Studies of Modifications of Solid Industrial Wastes* Progress Report, Part II, *Summary of Physical Properties of Solvay Industrial Waste Bed Materials,* Grant No. 5-R01-U1-00537-01A1, C. S. Grove, Jr., and L. J. Goodman, December 31, 1968, (Syracuse University, Syracuse, N. Y. 13210).

3. *Rehabilitation of Solid Industrial Wastes Disposal Sites,* Presented 24th Purdue Industrial Waste Conference, May 8, 1969, C. S. Grove, Jr., Mark L. Kestner and N. L. Nemerow under Grant No. 5-R01-U1-00537-01A1. (This paper is published in the Proceedings of This Conference, Part 2, Page 1072, Engineering Extension Series No. 135.)

4. *The Rehabilitation of the Solvay Process Waste Beds,* Grant No. 5-R01-U1-00257-02, C. S. Grove, Jr., F. W. Boecher, Chris Biemiller and W. H. Li, December 1, 1969, (Syracuse University, Syracuse, N. Y. 13210).

5. *Survey Review - Solid Wastes: Scope, Quality and Quantity,* Grant No. 5-R01-U1-00257-02, C. S. Grove, Jr., David Marlowe, Mohinder K, Saini, James Mandel, Charles M. Antoni, and N. L. Nemerow, December 1, 1969, (Syracuse University, Syracuse, N. Y. 13210).

6. *The Rehabilitation of the Solvay Process Waste Beds,* M. S. Thesis by F. W. Boecher under Grant No. EC-00257-03, June, 1970, (Syracuse University, Syracuse, N. Y. 13210).

7. *Survey Review - Solid Wastes: Scope, Quality and Quantity,* Grant No. EC-00257-03, C. S. Grove, Jr., David Marlowe, and C. M. Antoni, December, 1970, (Syracuse University, Syracuse, N. Y. 13210).

8. *Rehabilitation of Solvay Process Waste Beds,* by C. S. Grove, Jr., C. Biemiller and F. W. Boecher, presented at Symposium on Solid Industrial Wastes, Cincinnati, Ohio, May 1971, American Institute of Chemical Engineers: Based on Work under Grant No. EC-00257-03. (N.B. This was a slide presentation so no printed copies are available.) (Syracuse University, Syracuse, N. Y. 13210).

9. *Modifications of Solvay Process Solid Waste Disposal,* M.S. Thesis by R. J. Norwood under Grant No. EC-00257-03, June 1971, (Syracuse University, Syracuse, N. Y. 13210).

10. *Inhibition of Acid Mine Drainage by Municipal Solid Waste Effluents*, M. S. Thesis by Christopher C. Biemiller under Grant No. EC-00257-03, June 1971 (Syracuse University, Syracuse, N. Y. 13210).

11. *The Use of Solid Industrial Wastes in the Preparation of Construction Materials*, M.S. Thesis by Jyh-Chau Lin under Grant No. EC-00257-03, June 1971 (Syracuse University, Syracuse, N. Y. 13210).

12. *Effect of Humus Matter on Retention of Nitrogen Fertilizers in Soils*, M.S. Thesis by Mohinder Kumar Saini under Grant No. EC-00257-03, August 1971 (Syracuse University, Syracuse, N. Y. 13210).

MULTIPLE COPIES OF EACH OF THE REPORTS (WITH THE EXCEPTION ON NO. 8) WERE SUBMITTED TO THE OFFICE OF SOLID WASTES, NATIONAL ENVIRONMENTAL RESEARCH CENTER. THESE WERE LISTED WITH THE SOLID WASTE INFORMATION RETRIEVAL SYSTEM (SWIRS). NO COPIES OF ANY REPORT ARE AVAILABLE FROM THE AUTHORS. COPIES OF THE NAMED THESES ARE OBTAINABLE FROM THE SYRACUSE UNIVERSITY LIBRARY ON AN INTER-LIBRARY LOAN BASIS.

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# CHAPTER I. "STUDIES OF MODIFICATIONS OF SOLID INDUSTRIAL WASTES" PROGRESS REPORT, PART I, "COLLECTION AND ANALYSIS OF DATA ON SOLID INDUSTRIAL WASTES" C. S. GROVE, JR., N. L. NEMEROW, M. KESTNER, AND F. BOECHER (DECEMBER 31, 1968)

## A. Introduction

The scope of the solid industrial waste problem is complicated by many factors. Probably the most important and pertinent items in developing a grasp of the enormity of the industrial wastes are: (1) Lack of information available from many industries; and (2) Limited solicitation of positive data by concerned workers. Efforts were initiated to delineate some effective methods of obtaining positive and usable data.

## B. Initial Approaches to Data Solicitation

An initial letter of inquiry was prepared and sent to 98 industrial trade associations and selected individual manufacturing facilities. Although 63 responses were received of this letter of inquiry, only 25 furnished meaningful information.

Based upon results of the first solicitation, it was deemed necessary to broaden the inquiry by requesting data in a second letter addressed to universities, state and federal agencies involved in some form of solid waste management. Of a total mailing of 138 letters, 84 (61%) responses were received. Of these, 39 (27%) provided some helpful information.

The paucity of data obtained through the mail inquiries indicated that more direct personal contacts were necessary to elicit detailed information. A personal interview form was developed and tested on various industries in the Central New York area. It was found that a manufacturer or industry becomes more open in discussing solid waste problems and furnishing data on industrial production in a direct face-to-face interview. It was determined also that such interviews were very time consuming both for the investigator and for the person furnishing the replies.

Another potential source of quantities of solid industrial wastes appeared to be the private contract haulers. Several interviews with these contractors showed that data of value could be developed. However, the research team would need to ride the collection vehicles with the drivers if the data were to be reliable.

Detailed analyses of the favorable responses to the letters of inquiry and of the completed personal interviews are contained in the reference report.

## C. Projections of Industrial Solid Waste Characteristics

Projections of the total national production of industrial solid wastes appeared to be extrapolatable from data obtained on an individual basis. For example, the Feed Manufacturers Association reported that a 1000 pound cow produces 64 pounds of waste per day, consisting of 70% liquid and 30% solids. The World Almanac indicated that there were, in 1968, 108,491,000 dairy cows in the United States. This is a total of approximately $2.5\times10^{12}$ pounds of cattle waste per year (equivalent to $1.25\times10^{9}$ tons). Obviously, this projection does not include the wastes amassed in feed lots for cattle fattening. Similarly, national projections could be made for other agricultural wastes.

Another type of projection of total quantities of solid industrial wastes used as a basis the volume produced by an interviewed air conditioner manufacturer. This plant produced on an average 850 cubic yards of waste per day, amounting to an annual solid waste quantity of 310,000 cubic yards. This particular facility reportedly manufactures about 15% of the total national production. Based on these figures, a rough estimate of the total quantity of solid wastes by air conditioner manufacturers is 2 million cubic yards per year.

In many instances, industrial facilities simply do not have accurate data on solid waste quantities. Even when extensive data have been collected by an industrial complex it may not be made available. Typical of replies to solicitation inquiries is the following direct quote:

> "Quite frankly, the type of data you are after is very difficult to obtain and, in some instances, non-existent. At the present time, our organization is in the middle of a Company-wide survey to bracket in the solid waste area for the first time. We will soon know, for example, what types of solid wastes are generated at each plant, the amounts of each, current practice for on-site and off-site disposal, and costs of handling each type. Obtaining such a Company-wide account from over 200 different facilities is both time consuming and frustrating--even with our Company. When the above report is finished, unfortunately it will not be available for public consumption. It will, however, be used internally to keep our environmental releases within acceptable limits."

## D. Categories of Industrial Solid Wastes

There appears to be a broad categorization of industrial solid wastes: (a) Useful or reusable; and, (b) Presently not resuable (i.e., not recovered for reuse). Typical of category (a) is the exceedingly large tonnage of solid wastes from livestock and from chicken and egg production. This solid waste has an excellent value as humus and fertilizer. Solid industrial wastes from the aforementioned air conditioner manufacturer are divisible into reusable and not reusable catagories. The total tonnage (about 25%) of metal scrap is recovered and sold. The paper and other wastes (comprising about 80%) have to be carted away for disposal at a cost of about $100,000 per year. No effort is made to salvage paper or wood, as salvage seems uneconomical to the company.

Personal interviews prior to the initiation of this project indicated that industrial solid wastes totalled about 10 tons per day on a dry basis for a large plating plant and about 800 tons per day on a dry basis for a large chemical plant in the Syracuse area. None of this waste is presently recovered for any form of reuse. At present, each of these two solid wastes fall into Category (b). Yet the solid plating wastes contain over 4% of oxides of nickel, chromium, zinc and copper, with possible refractory brick properties.

A recent review of published data by M. Kestner ("Slag - Iron Blast Furnace," Syracuse University Seminar, M. L. Kestner, November, 1968) showed that in 1960 the total slag produced was equal to the total slag processed for other uses. In other words, slag from iron and steel production does not present an industrial solid waste problem. Even witn increased, as predicted, iron and steel production in the future, no problem is envisioned with this solid waste of Category (a).

## E. Theory of Diffusion and Leaching

Data and information developed initially have shown that one area of rehabilitation of industrial solid wastes depends on rate of diffusion of soluble salts and their final removal by leaching techniques. Neither diffusion nor leaching are practicable unless infiltration and percolation of waters are successfully carried out. Then, the rates of diffusion and leaching become functions of theoretical considerations and determination of coefficients and constants, experimentally derived on various wastes, with varying porosities, soluble salt concentrations, and chemical physical characteristics.

There are two extremes in theoretical concepts of diffusion and leaching: (1) Diffusion of completely soluble components with leaching from insoluble surroundings; and, (2) Chemical reaction of insoluble components to give soluble products with subsequent leaching from insoluble gangue materials. The first extreme is exemplified by the solid waste deposits of chemical industry, of the Solvay Industrial Chemical type, wherein about 30% are normally water soluble. The second extreme is typified by coal mine "over-burden" wastes in which there is a limited amount of soluble material until oxidation and/or carbonation furnish soluble products. The "acid" mine drainage from the coal mine tailings is typical of this extreme. In between, there is a range of highly soluble mixed in debris of poorly soluble and/or non-soluble materials.

The study of highly soluble materials in a matrix of insoluble residue is susceptable to theoretical consideration and design of experiments to verify diffusional theory and to determination of controlling coefficients. This is a condition of the first extreme and is applicable to many other industrial solid wastes. The other extreme requires a broader base with a combination of diffusion theory and chemical reaction leading to solubilization. Elucidation and verification of theory for the first extreme are essential to development and perfection of theory and experimental design for the second extreme.

## E. Initial Conclusions

The major conclusions developed during the initial study, as summarized above, are:

(a) Types, and therefore, quantities of industrial solid wastes can be conjectured, and, in some cases, determined from consideration of the products and production processes of various categories of industry.

(b) Quantities of industrial solid wastes cannot be determined by direct inquiry of any industry or of many industrial trade associations.

(c) Information and data on quantities of industrial solid wastes can be developed by a methodology of personal interviews and projections based on percentage share of market compared to national production figures.

(d) Development of a theory and experimental design for an industrial waste consisting of soluble and insoluble constituents appears very promising. At the other extreme involving chemical reaction to obtain solubilization of some constituent in a matrix of highly insoluble components, both theory and experimental design are less "clear-cut" and need much more background investigation.

## G. Tables and Charts

Tables and charts pertinent to the conclusions are presented in detail in the reference complete report.

# CHAPTER 2. "STUDIES OF MODIFICATIONS OF SOLID INDUSTRIAL WASTES" PROGRESS REPORT, PART II, "SUMMARY OF PHYSICAL PROPERTIES OF SOLVAY INDUSTRIAL WASTE BED MATERIALS" C. S. GROVE, JR. AND L. J. GOODMAN (DECEMBER 31, 1968)

## A. Introduction

The physical properties of the *Solvay industrial waste bed materials presented and discussed in this report were obtained from various sources including the files of the Bureau of Soil Mechanics, New York Department of Transportation, Albany, New York. The Bureau had to investigate and evaluate these physical properties from an engineering standpoint in connection with the design of highways to be built on this material as a part of the Onondaga Lake West Shore Development. Included in the files were innumerable drill hole or test boring logs and a report entitled, "Stability Investigation, Waste Bed No. 9" prepared by Evan W. Vaughan, Consulting Engineer, Syracuse, New York, for the Solvay Process Division, Allied Chemical and Dye Corporation. Attention was also devoted to a Master's Thesis by John Hewlett (College of Forestry, Syracuse University, June 1956) on the subject of "The Development of Vegetation of the Solvay Waste Beds".

## B. Description of Solvay Industrial Waste Bed Material

The State of New York Bureau of Soil Mechanics describes the Solvay Industrial Waste Bed Material as a white sludge with grey layers throughout. The consistency is described as varying from wet and soft to firm.

Vaughan describes the material in Waste Bed No. 9 as one which varies in general appearance and consistency from a sandy, fairly stiff substance

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* The Solvay industrial waste beds are deposits of solid wastes generated by Solvay Process Division (Now Industrial Chemical Division) of Allied Chemical Corporation, located on the shores of Onondaga Lake at Solvay, New York.

near the edge of the bed to a very soft, greasy, fine-grained material at the interior of the bed. The outer slope of the bed is composed of cinders, loosely placed. The waste, whether coarse or fine, is stratified and presents a banded appearance. This structure results from the hydraulic method of placement. Stratification is particularly evident in the sandy portion of the bed near the dike. Here the coarse and fine material occur in alternate layers, the coarse material predominating. The layers of fine waste are relatively thin but probably extend from the central portion of the bed to the dike. The State of New York Bureau of Soil Mechanics states that the waste is predominantly fine-grained, possibly as much as 90+% of the deposits investigated by their personnel. The coarse waste is due to sand size impurities, such as fly ash.

Hewlett notes that the subsoil beneath any cover soil is generally pure white, varying from a "putty-like to a cheesey," and sometimes to a firm chalky consistency. When exposed on a clean face it is slick to the touch. It is often thinly laminated, but at other times it is massive and uniform in structure. When the rooting zone is still shallow it may be broken by vertical cracks which have been filled with material from the surface, sometimes containing darkened organic matter. In the latter case, roots do not penetrate into the subsoil by way of these cracks.

## C. Discussion of Physical Properties of Solvay Industrial Waste Bed Material

The Solvay industrial waste bed material has unusual physical properties that must be considered in rehabilitation and beautification of the presently barren land areas covered by deposition of these industrial wastes. The material in question is a waste product of the Solvay process and consists of variable deposits of chemical by-products and impurities. The material is characteristically white or whitish-gray and generally has the consistency of soft cheese in the "in-place" condition after deposition. The structural strength of the waste bed material is apparently derived from a type of chemical bond between individual particles. A severe disturbance such as that caused by a shock wave can destroy this bond, causing the material to liquify and become a slurry-like substance with little or no shear strength. As a matter of fact, in 1943 a section of the dike retaining one of the waste beds failed and the material liquified and flowed out over the adjacent New York State Fairgrounds, including the highway and railroad.

The Solvay industrial waste bed materials are extremely compressible as evidenced from large void ratio values. In fact, it should be noted that the New York Bureau of Soil Mechanics personnel has observed that settlements greater than 2 feet are likely to occur where waste beds 20 to 28 feet in thickness are subjected to embankment heights greater than 6 feet. This is demonstrated in Figure 2 of the reference report which shows a plot of fill height versus settlement as obtained from field data. It is of interest to note that Figure 2 has the general appearance of a void ratio-log pressure plot from laboratory consolidation data.

The State of New York has also observed that the waste bed materials are four times as corrosive as sodium chloride. This is due to the calcium chloride content even with a high pH of 11. The waste is a deliquescent material which absorbs moisture. The natural moisture content ranges from 100± to 250±%. The liquid limit has a range of 72.4 to 235 and the plasticity index has a range of 5.8 to 68.3. In the majority of the test results the liquid limit is less than the natural water content which indicates that the material is extremely sensitive to a change in load. The normal range of the plasticity index is 25± to 60±.

There are no physical data on permeability characteristics of the waste bed material. However, available data from both field and laboratory studies indicate that the material is relatively impervious. The Vaughan report notes that the soft character of the waste in the bottom 5 feet of the bed (Waste Bed No. 9) indicates poor drainage in that region. Vaughan also notes that any significant drainage through the waste material occurs only when there are deep cracks or other openings extending through the waste bed to underlying pervious strata. He therefore recommends that adequate drainage of water be provided at the toe of the bed.

Hewlett's study was concerned with the development of vegetation in the abandoned waste beds along Onondaga Lake in connection with the feasibility of land restoration for public use. The study assessed the natural progress of vegetation growing on the beds and revealed 138 species of plants, fungi, and bryophytes. The most widespread grass observed was Poa Comprssa, while the most common trees and bushes were Scotch Pine, Weeping Birch, Cottonwood, Quaking Aspen and Purple Willow. Some attention was devoted to physical and chemical properties of the waste bed materials at shallow depths (0 to 20 inches). Moisture equivalents by the centrifuge method were found to range from 51 to 96%. Grain size analyses indicated a predominance of silt sizes (62 to 82%), little to some sand sizes (13 to 38%) and none to a trace of colloidal sizes (0 to 5%). It is not clear whether the clay sizes were included with the silt or colloidal sizes. Infiltration rates ranged from 5.8 to 65 inches per hour from surface tests on a barren area (with no surface cracks) and on an area supporting about 20% plant cover, respectively. A percolation rate of 0.3 inch per hour was recorded through the top 5 inches in the barren area.

## D. Initial Conclusions

Based on a review of available date, initial conclusions were drawn:

(a) It is concluded that a cover of topsoil or humus along with fertilization must be employed to support and improve the development of vegetation on any abandoned waste bed.

(b) It is also concluded that any abandoned waste beds can be utilized for development of relatively light industrial buildings, parking lots and highways. This has been demonstrated by successful constructions in the past on waste bed areas after many years of aging.

(c) It is further concluded that methods of improving infiltration and percolation must be developed so that soluble salts can be more rapidly removed. Complete removal or even partial removal will permit better settlement and will allow growth of more desirable vegetation.

## E. Tables and Charts

Tables and charts covering the developed data and pertinent to the conclusions are presented in full in the reference complete report.

# CHAPTER 3. "REHABILITATION OF SOLID INDUSTRIAL WASTE DISPOSAL SITES,"

C. S. GROVE, JR., MARK L. KESTNER AND N. L. NEMEROW,
PRESENTATION AT 24TH PURDUE INDUSTRIAL WASTE CONFERENCE
(MAY 8, 1969)

## A. Introduction

Solid industrial wastes arise from many different sources in a large variety of industries. As such they vary in quantity, physical and chemical properties, methods of disposal and potential re-uses. The major objectives of this research are: (1) To determine the quantities, physical and chemical properties of major solid industrial wastes; and (2) To study modifications of these properties that will permit useful by-product recovery or rehabilitation and beautification of the presently barren land areas covered by deposition of these wastes. To meet these objectives the following coordinated program was carried out: (1) Collect and collate the available information and data concerning quantities, characteristics, methods of disposal and potential re-uses of various solid industrial wastes; (2) Determine common physical and chemical properties and variants of the categorized wastes; (3) Project total national industrial solid waste production for selected groups of industries; and (4) Study methods and rates of infiltration, percolation and leaching, under simulated and natural conditions, for removal of valuable by-products and harmful or undesirable constituents which at present render the land areas covered by deposition of these wastes barren and unproductive.

## B. Methods for Collection of Industrial Solid Wastes Information

The methods used for collecting industrial solid wastes information included: (1) Letters of inquiry; (2) Personal interviews; and (3) Literature survey from 1960 to date. The letters of inquiry were circulated to various industries, universities, and state and federal agencies. Personal interviews were conducted to obtain more detailed information concerning quantities of solid waste production for particular manufacturers or processes. Personal interviews of the industrial waste haulers were conducted to provide additional information and checks on the accuracy of the information obtained from industry. The literature survey is concentrated on articles abstracted in *Engineering Index, Chemical Abstracts* and *Purdue Industrial Waste Conference Proceedings*. Information and data from many other sources also were sought by solicitation of bulletins and pamphlets and from journals in the broad area of solid wastes and their management. Many of the journals and newsletters were of recent origin and are not generally available to researchers.

Solid industrial wastes continue to increase in quantities each year. This is partly due to the increased demand for more production of useful materials. It is also a result in many operations such as mining to exhaustion of high grade ores and of the necessity to move into lower grade ores. As an example in 1965 the weight ratio of solid waste to marketable copper was 333.4; it is estimated that in 1980 this ratio will be 436.8.

Many new uses have been suggested for some of the solid industrial wastes. For example, fly ash has been used as a light-weight aggregate, as a soil neutralizer and as an aid to clarification of waste waters. Others appear to have little value under present economic conditions. Reworking of tailings from mines may be justified under new economics of exhaustion of high grade ore bodies.

As problems continue to increase on cost-benefits of land as a place for deposition of solid wastes or as a source of value to communities for building, for recreation, for highways and for other usages it becomes essential to ask the questions about types, quantities, methods of disposal and possible re-uses for all varieties of solid wastes. Land is not an inexhaustible natural resource; so polluted land must be returned to useful life by utilizing the complete spectrum of technical skills and local or national pride to bring about rehabilitation and reclamation of polluted land areas.

Details of the letters of inquiry and interview forms are fully presented in the report from which Chapter 1 was summarized. Results of the broadened literature survey are detailed in the report on which Chapter 5 was based. These reports as referenced are available only through the Solid Waste Information Retrieval System (SWIRS).

## C. Solid Waste Disposal Bed Modification and Rehabilitation

One form of land pollution is brought about by deposition of mixtures of inert and insoluble solids with varying amounts of soluble constituents. Modification of such a polluted land area involves removal of the soluble salts so that vegetation will grow without toxic conditions; of equal importance, stabilization of the area is necessary so that structures can be built without undue settlement. A study of this type of solid industrial wastes was undertaken.

Some solid wastes are highly saline containing diverse salts such as sodium chloride, calcium chloride, or sodium sulfate. Others are subject to oxidation leading to acid effluents, such as sulfide tailings of coal mines. Removal or reduction of these materials harmful to desirable plant life is essential to rehabilitation of the solid waste areas by growth of vegetation. Rapid removal of these soluble materials will also accelerate the consolidation of the waste bed, and eliminate prolonged seepage of undesirable solution from the bed and undue settlement. This phase of the investigation covered the study of the removal of these soluble materials by leaching with water.

A theoretical analysis of the removal of soluble compounds held in a matrix of insoluble and inert materials was developed. Some experimental investigations were carried out utilizing mixtures of high silica sand and a soluble salt such as copper sulfate. There are two difficulties in the theoretical study of this leaching problem: (1) The flow passages in a porous bed are randomly arranged; and, (2) A determination of the boundary conditions at the interface of any flowing solvent and the soluble solid are unknown. Details of the "Theory of Leaching" are shown in Section IV, pages 46 to 60, of the complete report on which Chapter 4 is based. (SWIRS should be contacted for the reference report.)

## D. Conclusions

(a) Types and, therefore, quality of industrial solid wastes can be conjectured, and, in many cases, determined from consideration of the products and production processes of various types of industry.

(b) Quantities of industrial solid wastes usually will not be disclosed fully by direct inquiry of any industry or of any industrial trade association. (Reluctance to divulge any information and data apparently arises from a well-publicized fear of local, state or federal regulations covering air, water and land pollutions; each of these areas of pollution are involved in disposal of industrial solid wastes.)

(c) Information and data concerning quantities, characteristics, and methods of disposal can be developed by a methodology consisting of: (1) correspondence; (2) literature survey; and (3) personal interview of company officials and industrial waste contract haulers.

(d) National solid wastes projections for some groups of industries can be determined based on: (1) amount of raw material processed; (2) total number of employees; and (3) percentage share of market the individual interviewed plant produces.

(e) Development of a theory and experimental design for an industrial waste consisting of soluble mixed in a matrix of insoluble constituents appears promising. At the other extreme, involving chemical reaction to obtain solubilization of some constituent in a matrix of highly insoluble components, both theory and experimental design are presently on less sound ground.

## E. Reference

The complete reference for this chapter and for the original paper is: Engineering Bulletin of Purdue University, Proceedings of the 24th Industrial Waste Conference, May 6-8, 1969; Part Two; Engineering Extension Series No. 135, pages 1072 to 1089.

## CHAPTER 4. "THE REHABILITATION OF THE SOLVAY PROCESS WASTE BEDS"

C. S. GROVE, JR., F. W. BOECHER, CHRISTOPHER BIEMILLER
AND W. H. LI (DECEMBER 1, 1969)

### A. Introduction

The Solvay process is a chemical process which produces soda ash; in the process vast amounts of solid wastes are also produced. The disposal of these wastes presents a major problem to the industry as well as to the community hosting it. When these wastes are disposed of on land they require large areas. Because of the character of the wastes these lands are rendered useless for many years.

Almost fifty percent of the waste is in the form of soluble solids. In order for these lands to become stable and usable they will have to reach a consolidated state. The leaching of the soluble materials has to occur and become almost complete. However, the waste is composed of very fine materials and drainage of water through it proceeds at a very slow rate. It is for this reason that the lands where these wastes are deposited become so useless for such a great length of time.

Two major methods of handling these wastes have been considered. The first involves trying to seal the surface of these beds once they have been filled in an attempt to keep the precipitated rain and snow from draining through the beds. This means keeping the beds as they are with no attempt to change their structure and composition. This method might have an advantage of making the beds usable immediately after they have been filled. One can also see many disadvantages connected with this solution. Water will always seep into the bed. It may enter either through cracks or failures in the covering or through seepage through the sides of the beds which are merely dikes made out of soil. The waste itself is in a very moist state; the drainage or drying of the waste over a period of time will carry out some of the soluble materials. Ground water in the area may also reach into the beds and slowly leach away the soluble constituents. There is also a factor to consider which concerns the capillary forces associated with the soluble materials. These may drain away themselves into moister areas over a period of time or move upwards into drier areas. It would appear that handling the waste disposal beds in this manner could be a very temporary solution. It would probably just slow the rate at which the beds would become completely stable after all the dissolvable materials are removed by various natural processes.

The second method of approach to this problem involves an effort to remove the soluble materials at a faster rate in order to obtain a stable insoluble material. At some particular plants this might be done in the plant before the waste reaches disposal. This method would require a thorough knowledge of the process at the particular plant. The present problem under investigation is the leaching of the wastes which already are in disposal beds occupying acres of land. If this can be accomplished many acres of now useless land area can be utilized in the near future. It is not expected that any large structures could be built on these wastes areas.

In order for these presently barren areas to become useful and stable the soluble salts must be removed. As the soluble materials are being dissolved out, even at the present slow rate they severely pollute the streams, rivers, and lakes into which they drain. This leach water is highly alkaline and contains a high content of solid material. Therefore, in rehabilitation of a waste bed by leaching, the rate of leaching must be carefully controlled.

## B. Background of Solvay Soda Ash Process

The Solvay soda ash process was developed during the latter part of the nineteenth century. It is described in detail by many authors, including Shreve (R. N. Shreve, *Chemical Process Industries*, McGraw-Hill, New York, 1956) and by Solvay Sales Corporation, *The Solvay Blue Book*, 1961.

In 1881 the Solvay Process Company was incorporated in New York to manufacture soda ash. The first plant was located at Solvay, near Syracuse, New York because of the contiguity of limestone and salt deposits. This plant began operations in 1884 with a daily production of about twenty tons. The Solvay Process Company is now known as the Industrial Chemical Division of the Allied Chemical Corporation.

## C. History of the Local Waste Beds Contiguous to Syracuse, New York

No information is available to indicate where the first waste was dumped when the Solvay Process Company began operations in 1884 near Syracuse; it is believed to have been somewhere along the southwestern shore of Onondaga Lake. Some of these early beds have been obliterated by construction. Parts of others still exist, and two or three retain their original outlines. Two of the oldest beds are indicated as the 1900 and 1902 beds. The data for the 1902 beds were substantially verified by employees of the Solvay Process Division of Allied Chemical Corporation. The data on the 1900 bed are estimates based on its position with respect to the 1902 bed and the recollections of a former employee of the company who first went to work on the waste beds shortly after the beginning of the century.

Farther up the western shore of Onondaga Lake, a new bed was begun about 1916, and presumably all of the older ones were abandoned at or before this time. This newer dumping area, called the Lakeside Beds, eventually covered approximately 365 acres. Seventy-five acres of this bed, immediately opposite the New York State Fair Grounds, were graveled and black-topped in 1954 for use as a parking lot. The adjacent banks were topsoiled to a depth of about ten inches and seeded.

The beds in active use are one-half mile inland from Onondaga Lake and cover what was formerly low land along Nine Mile Creek. There is no vegetation on the upper surface of these beds. A part of the 1902 Bed, still the property of the company, is being used as a settling trap for sludge by the city sewage disposal plant at the south end of the lake. Other than this, the more recently abandoned beds are not used for any purpose. The general sparseness of vegetation, the white glare of the ground and the heat in the summer, convey the idea of a desert to the casual visitor, who, once he has passed out of view of the Solvay industrial area, is struck by an odd sense of isolation.

During the process of building up the beds, segments of the total area were abandoned at several levels, leaving terraces of various sizes and ages around the perimeter. The amount of vegetation which has come in naturally on these segments varies according to the age of the particular segment. Some of the lower and older terraces are almost completely covered by a coarse type of vegetation while the upper and more recent terraces vary from barren spots to a thin covering of weeds and woody species. As these beds dried after abandonment, large and small cracks opened in the surface and traces of these cracks can be seen long after the phenomenon has ceased. Erosion is evident on nearly all surfaces of the beds, but the cutting of large gullies by surface flow is rather rare, as the retaining dikes tend to prevent their development.

Around the slopes, which are of various degress of steepness, there are occasional seepages of saline water. These seem to flow mostly in the late winter and spring, drying up completely in the summer. Some of the slopes show severe erosion while others are made up of partially cemented material which resists both erosion and the invasion of plant life. These latter slopes are the remains of the dikes used as sluicing channels and thus contain a great deal of the coarser materials from the waste. Those slopes which face eastward to the lake generally have more vegetation than those facing southwestward.

## D. Description of the Use of the Active Local Beds

The waste streams are pumped from the operating plant to the waste beds in a liquid slurry. The pipeline, at present, is several miles long leading to the nearest available land usable for disposal. When the pipeline reaches the beds which are lagoons held in by earthen retaining dikes the slurry is shunted through channels cut in the dikes around a section of the bed and then deposited on the surface. The coarser material quickly settles at the perimeter of the section of the bed; the remaining fine slurry fans out over the inner area. The sections of a bed in use are alternated periodically to allow the accumulated supernatant solution to drain. The period of "disuse" of any section of an active bed is about 24 hours. The bed is used normally until the deposited solids fill the volume available within the original dikes. When this dike level is reached a new layer of deposits is started by adding more earth and increasing the height of the dike. These layers are usually between four and five feet in thickness. The maximum height allowed by New York State is 60 feet for esthetic and practical reasons. This maximum height determines the base size required to maintain stability of the beds. The structural strength of the waste pyramid is apparently derived from some type of chemical bond between individual particles. This strength is not dependable because a severe disturbance, such as that caused by a shock wave can destroy the inter-particulate bond, permitting the material to be partially fluidized into a slurry with little or no shear strength. In 1943, a section of the dike retaining one of the older beds failed and the material not yet consolidated sufficiently, flowed out over the adjacent highway, railroad and the New York State Fairground's property.

## E. Composition of the Solid Wastes of the Local Solvay Process Plant

Representative samples were tested by the local Solvay industry. The samples were dried, passed through a 100 mesh screen, and analyzed by both wet chemical and X-ray methods. The tests indicated the following average composition, where the percent NaCl was determined by ionic imbalance, and the water of hydration was determined by difference:

| | |
|---|---|
| $R_2O_3$ . . . . . . . . . . . . . . . . | 6% |
| $SiO_2$ . . . . . . . . . . . . . . . . | 7% |
| $2CaO.SiO_2$ . . . . . . . . . . . . . | 17% |
| $CaCO_3$ . . . . . . . . . . . . . . . | 20% |
| $Ca(OH)_2$ . . . . . . . . . . . . . . | 4% |
| $CaSO_4$ . . . . . . . . . . . . . . . | 4% |
| $Mg(OH)_2$ . . . . . . . . . . . . . . | 10% |
| $CaO.CaCl_2$ . . . . . . . . . . . . . | 8% |
| NaCl . . . . . . . . . . . . . . . . | 6% |
| $CaCl_2$ . . . . . . . . . . . . . . . | 6% |
| $H_2O$ of hydration . . . . . . . . . . | 12% |

During the early stages of pumping into the waste beds, a large amount of liquid effluent drains through a stand-pipe arrangement. In the later stages drainage through the bed and into the adjacent waterway and eventually into Onondaga Lake is much slower. An average composition of waste bed effluent is shown below:

|  | Concentration mg/l |
|---|---|
| In Solution |  |
| Calcium chloride | 70,000 |
| Sodium chloride | 30,000 |
| Calcium carbonate | 100 |
| Calcium hydroxide | 600 |
| Calcium sulfate | 1,300 |
| Magnesium chloride | 30 |
| In Suspension |  |
| Calcium hydroxide | 50 |
| Calcium carbonate | 10 |
| Magnesium hydroxide | 25 |
| pH | 11.0 - 11.5 |

The physical properties of the solid wastes in the older Solvay disposal beds have been thoroughly discussed in the complete report on which Chapter 2 is based. There are only limited data on the properties of the newer disposal beds as no thorough soil mechanics study has been carried out. Initially, it appears that the soluble salts account for about 50% of the total dry weight of the solid wastes. Over a period of many years, slow infiltration of rain or snow precipitation reduces the amount of soluble constituents leaving voids which lead to settlement and slumping. Soluble materials are still slowly leaching out of the oldest disposal beds laid down along the southwestern edge of Onondaga Lake; these beds were started in 1884.

## F. Theory of Leaching

The problem for theoretical investigation is the removal of a soluble granular material in a porous solid waste bed by leaching with water. Leaching is accomplished by saturating the bed with water by flooding. The purpose of this theoretical study is to determine the rate of removal of the soluble material as affected by the various parameters involved.

To visualize the sequence of events during leaching, consider the case of a waste bed with a uniform distribution of a soluble salt. As the salt concentration of the water increases as it flows through the porous bed, the rate of dissolution of salt decreases along the flow. Thus, in the initial stage of leaching, the salt content of the bed decreases more rapidly near the entry of the fresh water. The salt content of the bed therefore becomes nonuniform and varies with time. This change of salt distribution in the bed in turn affects the salt concentration of the water. The problem, therefore, involves unsteady nonuniform mass transport. An exact solution of this problem is obviously difficult, if not impossible. To compound the complexity of the problem, the flow passages in a porous bed are randomly arranged, and the velocity distribution in these passages is unknown. Indeed, the solution of the differential equation involved is difficult even for much simpler problems.

As a first step to obtain a solution for predicting the rate of salt removal, the terminal Sherwood number (equivalent to Nusselt number in heat transfer) is studied. It must be noted that, in leaching, the terminal Sherwood number is reached within a very short distance, and its value can be considered to be dependent on the local condition of the waste material. Although this value may vary from one material condition to another, the variation is not large, and a value can be chosen for practical use. The effort of the initial stage of this theoretical investigation is therefore directed to seeking the terminal values of the Sherwood number for various salt content values. These values can then be used for computing the unsteady distribution of salt content in the waste bed during leaching.

To obtain an analytical solution for the Sherwood number, it is necessary to use a simpler model for the porous material with random passages. For this purpose, the porous material is represented by a group of parallelled small tubes with parts of the wall being soluble. It is believed that the terminal value of the Sherwood number of this model can be used for an equivalent porous material. Of course this model does not represent the porous bed in every aspect. For example, in a porous material, some dispersion of salt solution is caused by the randomness of the passages. This geometrical dispersion is absent in the flow through parallelled tubes. However, the rate of geometrical dispersion has been found to be only about 10% of the rate of dispersion due to nonuniform velocity distribution across the cross section of the passage. The error due to the absence of geometrical dispersion is therefore negligible in tubes with a nonuniform velocity distribution.

Based upon these assumptions, a theoretical equation was developed and methods elucidated for further simplification of the problem. Detailed mathematical procedures are shown in the reference report under "Theory of Leaching" (Pages 46 to 61).

A M.S. Thesis entitled "Theory of Leaching of Sensitive Non-soil Soils" is currently in progress by Mr. F. Feng under the direction of Dr. W. H. Li and Dr. C. S. Grove, Jr. Its completion is expected during the summer of 1972. When completed, a copy may be obtained on an Inter-Library Loan basis from Syracuse University, Syracuse, New York 13210.

## G. Experimental Study

The experimental study involved two categories: (1) Determination of the properties of the material and of the items involved in natural leaching of the solid waste disposal beds; (2) Development of methods of removal of the soluble constituents more rapidly. The following paragraphs summarize the experimental investigation:

(a) Tests were conducted with a soluble salt, copper sufate, mixed into an insoluble matrix of high silica sand. This mixture was placed under various concentrations in a vertically supported tube. Distilled water under a constant head was allowed to flow on the packed bed. Leaching of copper sulfate was observed.

(b) Determination of the physical characteristics of the Solvay process wastes was carried out utilizing three types of waste materials: (1) Coarse waste near the surface and edges of the new beds; (2) Fine waste from the center of the new beds; and, (3) Waste from the old beds from thirty to fifty years of age.

(c) Leaching characteristics of each type of waste were measured in vertical packed columns under a constant head of distilled water. Various materials such as digested sewage sludge, were added in order to improve the leaching. In one series of tests one normal sulfuric acid was tried as the leachant.

(d) Growth studies were made on several experiments in which a layer of the Solvay process waste was covered with topsoil and planted with grass seed. In one set of experiments, the container had no drainage holes; in the other drainage holes were provided at the bottom of the container. The change in salt concentration in the layers of topsoil as capillarity forces entered were observed, as well as the growth of grass.

The results of the experimental study were reported fully in the reference report (Pages 70 to 81).

## H. Summary and Conclusions

(a) The initial tests run with $CuSO_4$ demonstrated that a soluble material could be leached from an insoluble matrix. The major factor which determined the rate at which dissolution occurred were the grain size and void ratio of the insoluble matrix, as well as the grain size of the soluble material. The smaller crystals of $CuSO_4$ dissolved at a much faster rate than the larger crystals. It was also shown that the rate of dissolution decreased at a fairly constant rate from the time the distilled water was added until all of the $CuSO_4$ was dissolved. The greatest amount of $CuSO_4$ was dissolved rapidly and as the amount of available $CuSO_4$ decreased, the rate at which the $CuSO_4$ was being dissolved decreased.

(b) In the examination of the waste itself it was found that there were basically two types of particles present. There was a coarse grain and the second was finer grained in size. The vast majority of the waste beds consist of the fine grained material. The fine waste, which is the waste causing the leaching problems, has a grain size ranging from 10µ to 20µ and a soluble salt content of about 45%.

(c) The leaching of the waste proceeded at a slow rate; but it appears that if water is made available to the waste the solubles will be dissolved out. It has been concluded that the major problem involved deriving a way for the water to contact the soluble portions of the waste in a more rapid means. Also observed was that the greatest rate of leaching occurs at the outset of the run. It has further been observed that the rate of leaching decreases to almost a negligible rate after a short period of time and the amount of soluble material removed almost ceases. This leads one to conclude that there is channeling within the waste beds. Once the water has found a path to flow through and leaches the soluble material from it, it does not leach the remaining soluble materials very fast or well.

(d) Other observations made with respect to the leaching of the waste include the fact that the rate of water flow seems to decrease as the leaching proceeds. At the same time the waste in the columns does not settle at all. It would seem that once the solubles are dissolved out the void areas in the waste should increase and the rate of water flow should increase. The opposite is the case; the flow of water decreased. At this time one can speculate that some form of swelling may occur within the waste as the soluble solids leach out.

(e) It has been shown that with proper drainage facilities grass can be made to grow on tposoil covering the waste. This has been demonstrated with a generous flow of water. It has also been shown that there is a strong capillary force flow of solubles from the waste to the top soil layer.

## I. Recommendations

The following recommendations were made with respect to further experimentation that should be done on Solvay process waste bed materials:

(a) More information should be obtained on the bearing capacity of new wastes beds and that of the old beds. These values should be compared in order to determine how stable the beds become once the major portion of the soluble solids are removed.

(b) Further work on the growing capability of top soil placed on the beds should be investigated. These determinations should be more expansive than those obtained in the preliminary laboratory setups. A large plot, maybe 10 feet by 10 feet, should be investigated with respect to its growing ability with adequate drainage facilities provided.

(c) Further leaching experimentation with the waste should be performed. The intent of these further tests should be to explain why there is poor leaching and why the rate of leaching appears to decrease as the soluble particles are removed.

## J. Appendices

Photographs, figures and plotted data are shown fully in the complete report. A bibliography of 29 references is also appended.

# CHAPTER 5. "SURVEY REVIEW - SOLID WASTES: SCOPE, QUALITY AND QUANTITY" C. S. GROVE, JR., DAVID MARLOWE, MOHINDER K. SAINI, JAMES MANDEL, CHARLES M. ANTONI AND N. L. NEMEROW (DECEMBER 1, 1969)

## A. Introduction

The review of the literature on solid wastes which is digested in the first survey report covers material contained in four hundred and sixty-three references. The material surveyed may be divided into four major categories. The first is concerned with the types and quantities of waste produced by a variety of agencies both privately and publicly owned and operated. The second group concerns current and possible future collection and disposal practices while the third category emphasizes disposal through reclamation. In the fourth major section, a brief summary of some of the legislation in force at the time the report was prepared is given. The information digested in this report is assessed and evaluated and a tentative set of results and conclusions is presented.

## B. Solid Wastes

All literature on solid waste, including that concerned with waste disposal, is complicated because of the lack of standardization in the presentation of the data. Among the reports found particularly significant to this review were the following: (1) *Proceedings of the Symposium: Mineral Waste Utilization* Co-Sponsored by the U. S. Bureau of Mines and the Illinois Institute of Technology; and, (2) *Toward a Clean Environment* Survey of the Manufacturing Chemists Association. Fifth-three percent of the U. S. chemical industry disposes of its own waste, and in 1967 the industry reportedly produced 11 million tons of waste a year. Landfill accounts for 76% of the total solid chemical wastes disposal.

When refuse production is reported on the basis of number of workers, the values range from 5 to 10 pounds per worker per week in Textiles and Instruments, through 650 to 750 pounds per week in the Chemical and Lumber industries. The maximums are reported for Stone, Clay, and Glass of 1200 pounds per week and 2500 pounds per week in Petroleum and Coal. An attempt has been made to point up contradictions and anomolies in these data, particularly the low ratio of marketable production to refuse in the coal mining industry.

(a) Mining and Processing Wastes: Over the years 23 billion tons of mining wastes have accumulated of which 60% may have economic value because of mineral content or because of possible use as an aggregate. Thirty-seven percent have no value and constitute health and esthetic nuisances. The remaining 3% are too widely dispersed to constitute a nuisance or to serve a useful purpose. Production of these wastes is increasing; presently it is proceeding at the rate of 1 billion tons a year with estimates indicating a two-fold increase by 1980. No low grade waste is now processed to extract additional minerals because of cost, but it has potential for use as mine fill, land fill or highway fill.

(a-1) "Red Mud" produced in the extraction of aluminum from bauxite accumulates at a rate of 5 million tons a year creating water pollution problems. There is some hope that this waste may be a source of raw material for use in non-load bearing construction units.

(a-2) Copper Wastes are produced at an annual rate close to 500 million tons. The tailings are currently undergoing a stabilization treatment using vegetation to make them less visible and objectionable.

(a-3) Phosphate Mining Wastes are accumulating by 70 million tons per year. The waste, a 5% suspension of colloidal clay, does not solidify rapidly, and attempts to accelerate settlement of the solids have not been successful.

(b) Fly Ash: Production of fly ash from the generation of electricity using pulverized coal amounts to 25 million tons per year. While a number of uses for the material have been researched - as a substitute for cement, or a soil stabilizer, or a filler in asphalt, or a lightweight aggregate, as well as many other small scale uses, the potential market in the United States does not warrant the plant investment necessary. The large quantities produced indicate its disposal will be a continuing problem.

(c) Chemical Wastes are, in general, harmful to life, but a number of instances are presented in which research into specific treatment procedures yield innocuous waste and/or a valuable by-product. Research into other techniques may well be encouraged.

(d) Sludge from Liquid Wastes, such as sewage, has a moisture content of 75% or more and disposal takes many forms: incineration, soil spreading, evaporation, landfill, wells, fluidized bed incineration, the patented Zimpro wet air oxidation process, and the Porteous steam injection process. Sewage sludge may also be obtained from a sedimentation process and disposed of on landfill sites, or used as compost. Sludge is also produced in the pulp and paper, textile, tanning, dairy, chemical and pharmaceutical industries. These sludges usually have a stable composition as opposed to sewage sludges. In either case, organic sludges may be decomposed by aerobic or anaerobic microorganisms to produce a usable compost.

(e) Radioactive Wastes produced mainly in nuclear related industries require no treatment when radioactivity is less than $5 \times 10^{-5}$ microcuries per milliliter. Higher levels of radioactivity must be removed by some form of treatment. These wastes are currently stored in underground tanks or storage containers.

(f) Packaging Wastes are constituted of bottles, cans, wood, paper wrappings and paper board. The latter two make up more than 50% of all packaging waste. The waste from packaging amounted to 52 million tons in 1966 or 525 pounds per capita. It is anticipated this quantity will increase to 660 pounds per capita by 1976. Very little of this waste material is currently reclaimed or reused mainly because the amount of secondary materials - aluminum, steel, etc. - is far too scant for profitable salvage. A nationwide law to regulate the use and disposal of these packaging materials has been proposed, but the problems created outweigh the benefits at this time.

(g) Glass Industry Waste actually for the most part is the waste from the food and beverage industries. Being inert it causes no air, water or land pollution. The major problem is one of disposal. Research is concentrating on the production of a glass that will not break in use, but will crumble by intention, or a water soluble glass made impervious until broken when atmospheric moisture will cause it to dissolve.

(h) Rubber Wastes may be broken into three kinds: (1) Domestic, (2) Industrial, and (3) Discarded auto tires. The amount of domestic rubber waste is small - about 2% of the total - while industrial rubber waste and discarded automobile tires offer the possibility of reclamation. Unfortunately, while the quantity of tires discarded each year is increasing, the reclamation rate is decreasing, again because of cost. However, a coking type process for use on shredded tires produces chemicals, gas, and tar and shows some promise for the future.

(i) Junked automobiles constitute a waste causing serious land pollution. Currently 7 million vehicles go out of service each year, a sampling of which indicates that about 70% are at auto wreckers, 10% at scrap dealers, and 20% in auto graveyards. The inclusion of non-ferrous material with the iron contaminates it for primary use as ferrous scrap. Industrial scrap is more acceptable for steel production than that from autos, refrigerators, etc. Auto scrap may be reclaimed in the future through use in building materials or disposed of through a fusing with taconite to feed blast furnaces.

(j) Sanitary landfills, in which refuse is disposed by depositing it in this, compacted layers covered with earth at each day's end, constitute a major method for the disposal of municipal and industrial wastes. The organic wastes in the fill decompose anaerobically and careful management of the areas is necessary to minimize odors, vermin, and other undesirable effects. Costs range from $1.75 to $2.50 per ton depending on the length of haul. Landfills below the water table pollute the ground water. The disposal of industrial wastes at a sanitary landfill needs special attention to ensure that toxic, explosive, and fire hazards are recognized and guarded against. Planning for landfill operations is a problem and calls for careful engineering analyses involving alternate sites, population projections, estimates of the volume and character of the refuse, costs of not only site but also of hauling and operation.

(k) Incineration of solid waste requires high temperatures to reduce combustibles and other constituents in the waste to inert residues. Properly designed incinerators provide a nuisance-free, sanitary method of refuse disposal, but require a large capital investment and special equipment to meet air pollution standards. Only incineration and sanitary landfills give the flexibility necessary for solid waste disposal. Although landfills are less expensive, the increasing difficulty of finding suitable sites makes incineration more attractive especially in densely populated urban areas. Studies are underway to develop techniques for recovering the heat dissipated and the ferrous and non-ferrous metals left after incineration.

(l) The disposal of raw or treated wastes by dumping in the ocean has been a practice of urban areas for many years. Its adverse effects on marine life are becoming apparent and the imposition of restraints is necessary.

(m) Refuse disposal equipment is receiving increasing attention. Techniques are expanding to include flocculation to remove suspended solids in liquid waste, processing units to remove salvageable materials and to grind and compost the remainder, compacting equipment that coats the resulting solid block for use as fill, equipment for turning compost material and flexible rubber tanks to store peak sewage flow for treatment during off-peak hours.

(n) Air pollution occurs when one or more contaminants is present in the atmosphere in sufficient quantity to be injurious to life or property. It may occur in the form of smoke, dust, fumes, radioactive wastes and gases and may be generated from incineration, coal burning furnaces or coal refuse piles, or any other open burning operation ranging from the burning of agricultural products to the burning of insulation off copper wires. Levels of particulate emission permitted are given, and the efficiency of various types of control equipment tabulated in the original report.

(o) Thermal pollution of a body of water is the result of the process by which water is taken from a lake or stream, used as cooling water and returned at a higher temperature harmfully affecting aquatic life. The thermal pollution of waterways may be reduced through the use of cooling towers.

(p) Biological vectors in solid waste are those living agents that directly or indirectly transport diseases. A comprehensive discussion is presented of the relationship between biological vectors and solid waste with respect to fecal wastes, flies, bacterial and viral infections, rodents, mosquitoes and fungi.

(q) Composting is a biochemical process for the treatment of the organic materials in solid waste and changes them into a humus like product. In the process, it is desirable to mix industrial waste with municipal waste to yield the proper combination or organic and inorganic materials for a satisfactory result. The procedure is especially useful for the disposal of fluid whey, canning wastes, and meat processing wastes. A table lists industrial waste suitable for composting in the reference report.

## C. Current Collection and Disposal Practices for Solid Wastes

The methods used for collecting solid waste today make it difficult and even futile to distinguish between industrial and municipal wastes because they are either intermingled during collection or disposed of at the same sites. Only when an industrial plant uses its own facilities and land for final disposal is it possible to make the distinction.

The collection and disposal practices for solid wastes currently in use are covered in two books available from the Public Administration Service, 1313 East 60th Street, Chicago, Illinois 60637. They are: (1) *Refuse Collection Practice,* and (2) *Municipal Refuse Disposal.*

## D. New Collection and Disposal Practices

Refuse collection is commonly performed by trucks with multi-man crews and accounts for 70 to 80% of the $3 billion annual cost of refuse disposal. A systems approach in which field data are used for a computer simulation of the collection process has been attempted to increase its efficiency. The simulation resulted in recommendations to use one man crews for alley or curbside collection, multi-man for backyard collection, side loading compaction vehicles, and disposable containers for household uses. In addition optimization techniques are being used to plan efficient collection routes.

A national survey indicated that the 3 man crew and rear loading vehicle were in most common use, that the one man system may become more popular in the face of strikes even though it will require higher personnel standards, higher salaries, opportunities for advancement, and engineering evaluation of routes and equipment.

Transporting solid waste in pipelines is being studied, and in a model suburb of Stockholm is proving feasible for the collection of refuse from 5000 apartments. If a slurry system is contemplated, the problem of presizing becomes important. Various presizing units are available. The use of solid waste pipelines will, of course, depend on cost relative to a truck collection system.

## E. Reclamation and Re-Use Practices for Solid Wastes

A successful waste recovery program requires that garbage, combustible rubbish and non-combustible rubbish be collected separately, and depends on a sympathetic, well-informed public. These conclusions result from a study of waste collection in Los Angeles, and a set of tables in the reference report presents the composition of waste as determined during the study.

A number of items in solid waste offer potential for reclamation including greases for conversion to soap, waste paper for recycling, and food waste for composting. Rags, wood, and scrap metals also have good potential for processing and reuse in one form or another and, in fact, are presently separated from refuse for recycling. It is also profitable to salvage cast iron, and attempts are being made to recycle the aluminum in beverage containers. Federal law, public apathy, and cost act as inhibitors.

Packaging materials form 10 to 15% of the refuse problem. In 1967, packaging consisted of 30% metal, 30% paper and fiber, 13% glass, 13% flexible materials, 4% plastics, and 10% miscellaneous. The psychology, sales appeal, and other factors involved in packaging foods, beverages, and other items illustrate the difficulties involved in changing consumer and retailer habits away from non-returnable to returnable containers among other factors involved in this aspect of refuse disposal. Estimates are presented for the quantities of glass containers, metal cans, paper packaging, plastic containers, and synthetic fibers to be generated in the future in the original report.

As the quantities of waste increase, the continued resort to outdated methods for the management of its disposal exacerbates the problem. Landfills are not properly operated, settle, trap liquids, and gases, and their use is limited with the developing scarcity of suitable sites. An attempt is being made to accelerate decomposition to reduce settlement problems, but general use of the scheme may be impractical.

Grinding of the refuse may offer a temporary palliative and can be applied to landfill, incineration, and composting. More attention needs to be given to composting, particularly to encourage the use of compost as fertilizer but the requirement that the operations show a profit must be removed.

Various methods of retrieving mining waste, glass, copper, tin cans, and other minerals are under investigation and experimental techniques are described. Cement copper may be precipitated from acidic sulfate solutions using shredded automobile steel scrap in a rotary drum and appears to be competitive with the launder method in which detinned tinplate scrap is used. Zinc-base die cast scrap containing aluminum may be purified and refined by mixing with other secondary zinc products, but alternate schemes utilizing low cost fluxes are under investigation. The use of taconite ores with scrap from discarded automobiles is being pursued in an effort to expand the nation's resources while finding a use for a scrap product no longer in favor in the steel making industry. Other attempts to utilize the auto scrap involve separating the ferrous materials. The procedures include flotation methods, induction melting, reduction roasting, and electrolysis.

Further uses of fly ash may be available through processing for use as an aggregate and for the manufacture of bricks. The ash also has some value in chemical coagulation to clear turbid water. Fly ash and certain varieties of coal show promise in the removal of organic contaminants from the waste water of secondary sewage treatment plants.

Wood wastes in the form of sawdust, tree bark, and the other wood wastes of society may be reclaimed also: sawdust into kraft pulp, tree bark into waxes and phenolic compounds, and the other wastes carbonized, briquetted and sold as fuel. The conversion of dead city trees or broken and pruned limbs into chips provides one city's parks department with mulch needed to maintain its public gardens.

Several new methods for separating and/or treating solid waste are coming to the fore. One piece of equipment, the Hydropulper, removes heavy non-pulpable items; the remainder is disintegrated and pulped and removed from the pulper as a liquid suspension. It is then treated in a cyclone to remove the inert materials. The remainder is dewatered and fed to a fluid bed oxidizer. The heavy material, the inert material, and the residue from the oxidizer are disposed of as land fill. Paper, which may be recycled and which constitutes a large portion of the waste, may be partially reclaimed through a Fiber-reclaimer used in conjunction with the system. Costs are estimated to be midway between land fill and incineration. The system has the adaptability to combine with the municipal sewerage system, and may be refined further to reclaim metal and glass.

Another technique in use shreds solid waste ranging in size from glass and plastic bottles to automobile bodies. This is a staged process and offers the opportunity to remove non-ferrous metals by hand. These shredders produce a fine ground waste which occupies considerably less volume than the untreated raw refuse.

Waste paper, specially treated and formed, is being used to fabricate low cost housing units. Other waste materials may be used to develop new building materials - many schemes are proposed in this area.

To implement many of the techniques, ideas, and reuses for solid wastes it appears necessary that: (1) solid waste be sorted at its source; and (2) new materials and products be developed to create a demand for solid waste. However, the astronomical totals of fly ash, refuse, and other solid wastes produced in the United States present a disposal problem in which reclamation and reuse, or new products can make only limited inroads at this time.

## F. Legislation Covering Solid Wastes

At the time of this report public concern with air and water pollution, and failure to appreciate the land pollution resulting from solid waste disposal, prevented a large body of legislation from being enacted that would control solid waste disposal. In 1965 the Federal Government enacted into law the Solid Waste Disposal Act to assist financially in the development and application of new and improved methods to reduce the amount of solid waste and to provide economical and proper disposal methods. The Act contains many detailed provisions to carry out these objectives. This act was extended and expanded by legislation in 1969. Much of the initiative for implementing the

Act rests with state and local governments, and a list of suggestions for such legislation are tabulated. Local authorities should be given the power, among others, to:

(1) Establish an areawide solid wastes management system;

(2) Adopt requirements for the transport, storage, processing and disposal of solid wastes;

(3) Contract with public and private parties for collection and disposal;

(4) Acquire land for solid waste facilities; and,

(5) Finance a solid waste management system.

## G. Results, Conclusions and Recommendations

(a) The scope of the solid waste problem is many times larger than stated even by pessimistic observers.

(b) A direct approach provides the best method for obtaining solid waste information from industry.

(c) Emphasis on reclamation and re-use is increasing although landfill is still the major disposal method.

## H. Tables and Appendices

Detailed data on solid wastes produced in the chemical industry, the glass industry, general trash and its constituents, domestic refuse, mineral wastes, wood and paper wastes and organic waste are presented in the tables following the conclusions and recommendations in the reference report.

The Appendices describe the letters and personal interview forms used to collect information about solid waste production from industry and other sources. Attached, also, is a list of the correspondants solicited using these letters and forms.

Finally, the complete bibliography used in the preparation of the survey review is appended to the reference report.

# CHAPTER 6. "THE REHABILITATION OF THE SOLVAY PROCESS WASTE BEDS"

M. S. THESIS, F. W. BOECHER (JUNE 1970)

## A. Introduction

The Solvay process produces soda ash by a series of chemical reactions. The process results in large amountsof solid wastes, which are disposed of on solid waste disposal beds. The wastes are constituted of about 50% soluble materials in an insoluble matrix. This matrix is composed of very fine grains and consequently, drainage of water through it and leaching of the soluble portions proceed at very slow rates.

The main objective of the research is to find a method of increasing the rate of drainage through the beds in order that the soluble materials can be leached out at a faster rate. Should this objective be realized, many acres of now useless land area could be put back into use in the near future. It is not expected, however, that any large structures could be built on these waste areas.

In order for these large areas of Solvay process disposal sites to become useful, the soluble materials must be removed by leaching. Such action will permit consolidation of the areas for building of playgrounds, parks, golf courses or small, lightweight structures. Removal of the salts toxic to vegetation will allow such growth in a superimposed layer of topsoil.

In attempting to solve this problem, the rate of leaching of the beds was observed and the reasons for its present slow rate were investigated. The growing utilization and capability of these beds was determined partly. It is hoped that after studying these areas a better method of disposal for the wastes can be found so that in these days of growing urban development, vast areas of what could be useful land will not remain idle.

This study was a continuation of the work described in Chapter 4. It was carried out in greater depth in order further to elucidate some of the leaching problems and to evaluate some growth concepts.

## B. Background of Solvay Soda Ash Process

The background of the Solvay soda ash process is reviewed in detail under the following sections: a. Description of the process; b. The Syracuse works; c. History of the local wastes beds; d. Description of the use of the active beds; e. Composition of the Solvay wastes; f. Physical and Chemical characteristics of the solid wastes; g. Soil mechanics properties of the waste beds; and, h. Drainage of the waste beds.

Some of these topics are summarized in Chapter 4. Complete details are furnished in the reference thesis on which this chapter is based, pages 3 to 30.

## C. Background Review

The following topics are covered in this review: a. Theory of leaching; b. Drainage methods; e. Capillarity; d. Characteristics and quantities of typical chemical data; and, e. Review of some pertinent fact studies. Some of these topics are summarized in Chapter 4; others are detailed in the following paragraphs.

Drainage may be accomplished by a variety of methods. Ditches or tunnels may be constructed within a soil system with a gravity outlet (drainage by gravity) or by pumping from wells or ditches (drainage by pumping) or by surface evaporation (drainage by desiccation). The drained or excess water may escape along straight, parallelled lines (linear drainage), in radial planes (radial drainage) or by flow along lines having a three dimensional curvature (general case of a three-dimensional drainage).

The time required to drain the major part of the excess water out of the soil is called the rate of drainage. For a particular drainage system the rate and the effect of drainage both depend on the physical characteristics of the soil subject to drainage, such as grain size and compressibility. These characteristics range between the two limits represented by those of ideal sand and ideal clay. Since the waste in question more closely resembles a clay than a sand, it will be considered in the clay category.

Terzaghi defines the term ideal clay as "a highly compressible soil whose voids are so small that they remain completely filled with water during the entire process of drainage, provided the surface of the soil is protected against evaporation. Hence, the total volume of the water which drains out of the ideal clay is equal to the simultaneous decrease in the total volume of the voids".

Peck, Hanson, and Thornburn state that it is not possible to drain fine-grained soils, like clay, in a reasonable length of time by gravity alone. However, the drainage may be effected by desiccation and the moisture may be gradually lost by evaporation. They further state: "As the water evaporates, the solid soil particles are drawn into closer and closer contact on account of the surface tension of the water. At the shrinkage limit the strength of the soil is great enough to withstand the forces of surface tension without further consolidation, and, if further desiccation takes place, the process of an invasion begins. The moisture content does not decrease to zero but attains a value in equilibrium with the relative humidity of the soil atmosphere."

Many means of drainage have been developed and used. The major means of subsurface drainage employs the use of drainage tile. Sutton gives the design criteria and specifications for various types of drain tiles. He states that the soils being drained must be permeable enough to permit an economical spacing of drains. In laying drain pipe a small gap is left between the ends of the tile to permit water to enter the tile. Bell-end and tongue and groove pipe are used most extensively.

Silts and clay soils are estimated to have as much as five foot capillary heads. As the grain size diminishes the capillary forces increase. The forces of capillarity are directly interrelated to the phenomena of drainage and leaching in soils. It is the surface tension of the liquid for the soil particle surfaces that determines the amount of capillarity. Liquids have a tendency to wet the surfaces they contact. Wetting causes a physical curvature of the liquid surface and results in a contact angle between the liquid surface and the solid particle differing from $90^0$. An example of this phenomenon is the rise of water in a narrow glass tube. The contact angle between the two is zero. The total capillary rise decreases with increasing grain size for equal capillary pressures. As capillary heads increase with decreasing grain size the actual capillary rise per unit length of time is maximum at an intermediate grain size in the fine silt grouping.

Capillary forces are independent of atmospheric pressure and heads may exceed the thirty foot limit associated with typical suction heads. As a result capillary pressures calculated in fine grained soils can be tremendous: i.e., 100,000 $lbs/ft^2$. Soils subjected to such pressure for any length of time will consolidate to an extent that they may make excellent bearing materials.

In the case of the Solvay process waste material the relative rates of consolidation of the entire waste material versus the rate of solution of the dissolvable salts will determine the time required for rehabilitation of the beds. These relative rates need to be determined. The nature of capillary rise in a fine grained material may be either beneficial or detrimental.

As far as rehabilitation of solid waste beds, consisting of mixtures of soluble and insoluble materials, is concerned, capillarity opposes leaching and removal of soluble salts which may be (and usually are) toxic to growing vegetation. In other words, the forces leading to leaching must be strong enough to overcome the forces of capillarity that lead to excessive salinity and toxicity of the soil layer on which vegetation is attempting to exist.

Efforts to deal with the problem are directed toward the reasons the waste beds are so difficult to rehabilitate, and to gain insight into potentially inexpensive and expedient measures that may be taken to solve the problems. Sampling old waste beds and comparing the properties of these samples to the properties of the materials taken from recently deposited beds leads to the conclusions that the major problems are high moisture contents and high levels of soluble materials which excessively delay the appearance of what one might call a final inert and desirable condition. Each of these problems is bound to the soil problems of leaching rates, soil drainage, the interparticle capillary forces retaining waters of adsorption, adsorption and entrapment, and hydrostatic pressures.

The relative surface activity of a particle increases as its size decreases. A greater cohesiveness or adhesiveness will increase in proportion to the electrostatic inter-attractions which in turn are proportional to the relative surface area. The specific surface area of a particle varies directly with the change in the particle size. The specific surface energy for a given solid can multiply over 8000 times in going from a 2-mesh size to a one-mesh size. Thus the more a particle is subdivided the greater effect the surface energy can have on flow properties.

The tendency of a particle to hold water at the surface makes for accelerated massing, the surfaces thereby being more deformable. The high surface tension of the water film creates a more cohesive mass which may be easier to transport but infinitely more difficult to leach. The critical humidity of particular materials is of interest because of the effects on the mass of the absorbed water.

Free flow characteristics are improved with large sized particles with the resultant smaller external surface area, low surface activity, high free surface energy, hard and rough shape, and high density. The properties of bulk solids are the summations of the properties of the discrete particles individually. The bulk properties are more often discussed in terms of the parameters of bulk density, porosity, angles of flow, compressibility, cohesion, size and frequency distribution.

The study of the wastes from the Solvay process industries shows that the effects of weathering, leaching and drainage cannot be separated from disposal practices; the secondary effects are important and must be studied in terms of prevention or benefit. The failure of the waste beds to be reclaimed as good foundation sites for a sewage treatment plant and a highway has been described.

An ecological study of the development of vegetation on the above mentioned waste beds was conducted during the year of 1955. The beds will eventually occupy approximately 1100 acres of valuable suburban land. No complete proposals for the rehabilitation of the land have yet been offered. Invasion by plants brings about an alteration of the environment by the improvement of aeration and the reduction in salt concentrations in the surface layers. This results in the gradual deepening of the weathered layer of waste to which plant roots are narrowly restricted. The rate of deepening is rapid at first, reaching a peak in twenty years and progressing more slowly thereafter. Early plant succession is directly related to this lowering of the rooting limit.

The alkalinity of the waste beds and the high concentration of calcium ions tend to render phosphorous almost totally inaccessible to plants. This in turn prevents the build-up of nitrogenous organic material, and also maintains a nitrogen limiting factor in growth succession. In the chronological order in which they are believed to affect succession, the chief limiting factors are as follows: initially the soluble salt concentrations delay any invasion by plants; secondly, the limitation of rooting depth by the toxicity and lack of aeration in the subsoil prevents the coverage and protection of the ground surfaces; thirdly, the lack of available phosphorous prevents the build-up of available nitrogen by limiting the quality and quantity of plant cover.

Any management approach, in view of the high costs of reclamation, should consider possible measures prior to abandonment which might speed early and successful establishment of vegetation. Almost any over-all reclamation plan, even that of mass top soiling, should be approached with caution, and any methods adopted should be supported by actual experimentation on the beds before being applied on a major scale.

Complete discussion of the various topics is furnished in the reference thesis on which this chapter is based, pages 37 to 57.

### D. Experimental Works and Results

The experimental work in this study was an expanded continuation of the work summarized in Chapter 4. Full details are given in the reference thesis, pages 72 to 82. The results of the experimental work are presented in the reference document in full detail, pages 83 to 97 with a discussion of results on pages 98 to 102.

## E. Conclusions

Based upon the several experimental studies and comparisons with background review information and data, it was concluded that:

(a.) The waste can be leached and drained if adequate drainage is supplied in the form of sand drains and drainage tiles.

(b.) Vegetation can be supported on top soil over the waste beds if proper drainage is supplied and maintained.

(c.) The soluble portion of the waste can be removed if proper drainage for the water is made available and the surface of the waste is disturbed periodically.

(d.) The waste is a soft, sensitive material resembling a clay that can never be expected to support large structures.

(e.) The rehabilitation of this waste can be accomplished to support parks, golf courses, and other low-load bearing facilities if proper drainage facilities are furnished and maintained.

## F. Recommendations for Future Work

The following recommendations are made for further experimentation concerning the Solvay process waste beds:

(a) An in-depth study to find the most efficient location and spacing of drain tiles and sand drains to insure adequate drainage.

(b) The reasons and causes for the phenomenon that occurs on the surface of the waste and retards the infiltration of water.

(c) More comprehensive studies on the growing potential of top soil on the waste to be done at the site of the waste beds.

(d) Further studies into the sensitivity of the waste and how it compares to conventional clay soils.

## G. References and Appendices

The reference thesis on thich this chapter is based lists 33 pertinent references (pages 105 to 107) and 19 bibliographic readings (pages 108 and 109). Appendix A shows photographs of various portions of the overall Solvay process operations (Figures 1 to 17). Appendix B lists plotted experimental data for seven of the laboratory tests.

The complete reference thesis is available through the Solid Waste Information Retrieval System (SWIRS) or on an Inter-Library Loan from Syracuse University.

## CHAPTER 7. "SURVEY REVIEW - SOLID WASTES: SCOPE, QUALITY, QUANTITY" C. S. GROVE, JR., DAVID MARLOWE AND C. M. ANTONI (DECEMBER 1970)

### A. Introduction

The survey review of the literature, practices, and other aspects of solid waste and its management has been divided into four parts in an effort to provide some continuity to a series of apparently disconnected topics. In the first three parts, the effect of solid waste and its indiscriminate disposal on the environmental factors concerned with pollution of water, air, and the land itself is considered. The fourth sub-division is concerned with suggestions, pilot programs and implemented approaches for the solution to the pollution problems created by solid wastes.

Water pollution may be caused by the disposal of solid wastes in running streams, through the leaching from solid waste disposal areas of undesirable solutes, from the growth of undesirable plant life in the streams, from the disposal of dissolved solid wastes from chemical and other industrial plants and the deposition of soil and silt from eroded land. Many of these types of water pollutants are dangerous and prove extremely difficult to remove or neutralize in the waters to which they are discharged.

The atmosphere may also be polluted by solid wastes: fine particles resulting from combustion, wind blown silt, radioactive particles from nuclear explosions or, in fact, by any fine solid particles that are capable of being suspended in the air.

The land itself is rapidly becoming polluted through the disposal of solid wastes in land fill sites and the careless use of the land in other disposition methods.

During the course of collecting the information presented in this review, disparate items concerning quantities, sources, legislation, and proposed remedies have been brought together in an attempt to present as much available data on the four subdivisions of the report as possible.

## B. Air Pollution

Methods for measuring odors, an approach to quantifying air pollution, have not been standardized. A.S.T.M. has set up a standard method which involves the measurement of the dilution necessary to reduce the odor to the sensory threshold level. This approach is useful for industrial sources; non-confined sources, such as lagoons, will require different approaches. Odor measurements prove difficult to duplicate, but in any case odors are annoying and frequently are dangerous to man and other life.

In 1967 estimates of atmospheric contaminants on a yearly basis listed carbon monoxide at 72 million tons, sulphur oxides at 26 million tons, nitrogen oxides 13 million tons, hydrocarbons 19 million tons and particulate matter at 11 million tons.

Sulphur oxides are troublesome to people with respiratory problems. This contaminant is added to the atmosphere largely through the combustion of fossil fuels. Sixty percent of the sulphur oxide contaminants come from coal, and 80 percent of that is from power plants. Low sulphur coal, in 1964, amounted to 30 to 35 percent of the U. S. coal mined, 1/4 of it was for export, and most of the rest for metallurgical purposes. Limits on sulphur content is posing and will continue to pose serious problems to the power industry.

The removal of sulphur from oil fuels is less of a problem than from coal. The technology for desulphurizing distillate oils is available and although problems exist with residual oils, they are not insurmountable.

Coals contain sulphur as pyrite and as complex organic substances. Pyrite may be removed by grinding and washing, but organic sulphur requires expensive hydrogenation and liquefaction. Segregation of the coal by contaminant is difficult. When coal is burned, limestone injection and scrubbing are efficacious in removing solid particles of sulphite, sulphate, and most of the sulphur oxides.

Fly ash which is also released to the atmosphere from burning coal is now produced in large quantities but future production is uncertain because the power industry is being pressured to reduce air and water pollution, and is turning to other types of fuel. Some are committed to nuclear power, others to fuel oil. Production of fly ash, bottom ash, and bottom clay is expected to reach a total annual rate of 42.5 million tons by 1975 and, if the current rate of increase continues, 52 million tons per year by 1980. Air pollution control devices should be in general use by 1975 and will probably change the characteristics of this waste. Ash in all of its forms is used in the cement industry and for fill in roadbuilding and other construction processes. Utilization in the past six years ranges from 12 to 17 percent of total production. The rest constitutes solid waste which must be disposed of.

Considerable research has been undertaken to determine the best methods for the use of fly ash as an aggregate or cement replacement in concrete. Its uses have spanned more than 2000 years including road paving, and dam construction. A.S.T.M. specifications are available for the use of fly ash as a concrete admixture. Many factors control the characteristics of fly ash for use in concrete and these must be understood by the producers if a more extensive use of the material is to occur. Consistent correlations have been obtained between the relative water requirement and each of several fly ash variables: fineness, ignition loss, carbon, and specific gravity. Variations in the chemistry of the ash also have significance. However, no simple test has been found from the results of which fly ash performance may be predicted.

Fly ash may have use as a filler for bituminous materials. In this application it is important to take into consideration particle size and distribution, hardness, strength, specific gravity, and surface area.

A study of structural ceramics using fly ash was also instituted. One outgrowth was the production of building bricks, and another the fusion forming of fly ash mixtures. In this context, glass ceramic compositions have resulted in a number of novel applications such as chemically machinable glass, radomes and other electronic products, and those in which strength, hardness, and abrasion resistance greater than glass are important.

The injection of limestone for the control of sulphur oxides, and fluidized bed combustion result in new types of fly ash with changed properties which will call for continued study if the ash is to be salvaged in any large quantity. The Coal Research Bureau is investigating the recovery of unspent lime in limestone modified fly ash for reinjection into the boilers with the portion not reinjected subsequently used to manufacture mineral wool.

Fly ash, siliconized by treating it with silanes or silicones, has been used to control oil pollution at sea, an admixture for concrete, and proposed for use as a means of controlling water flow through soils, insulation for underground pipes, and as an anti-caking filler for powder and bitumen.

Those lightweight fly ash particles called cenospheres are in use as a coolant in foreign steel mills, while regular ash is in limited use in the U. S. to extinguish mine fires, control spontaneous combustion, combat mine subsidence, replace foundry core sand, and as an admixture in masonry mortar and in acoustical or insulating blocks. Some applicability for the use of fly ash as a water purifier, a soil modifier, and an aid in dewatering sewage sludge has also been demonstrated.

Other kinds of air pollution control involve reduction of contaminants from incineration through redesign of incinerators, and the reduction of sewage lagoon odors through collection and combustion of the gases emitted. One of the new incinerator designs was for the City of Stamford, Connecticut, and provided for the complete combustion of soot and hydrocarbons. Ash and particles are removed to leave a flue gas at least 95 percent clear.

### C. Water Pollution

Concern about the effects of water pollution is causing public officials at all levels, industry, and private citizens to take action to alleviate the problems it creates. A private citizen endowed a foundation to convert pollution in Lake Erie; Canada closed a new phosphorus plant because its effluent was damaging to stream life, and the State of Pennsylvania is reviewing landfill operations to determine the extent to which they contribute to water pollution and to devise corrections.

Soil erosion constitutes a major pollution problem. Public Law 556 appears to be applicable to this problem, especially if harmful effects are alleviated by proper grading of cuts and fills, use of mulches or natural vegetation and the use of diversion ditches. Helpful in these solutions are charts and other data concerning distribution of rainfall causing erosion of the soil. The magnitude of the problem is illustrated through presentation of the data for the Potomac River Basin where an average annual sediment rate of 170 tons per square mile for the entire area is composed of rates of 15 tons per square mile in native vegetaged areas, 100 to 400 tons per square mile in rural areas, and up to 50,000 tons per square mile in areas undergoing intensive urban development.

A number of unusual problems in waste treatment and disposal are presented. Leesburg, Florida is treating a combination of sewage and citrus waste in a specifically designed plant. Grand Rapids, Nebraska combines slaughtering wastes with municipal sewage and treats the mixture with activated sludge.

Pollution that results from industrial processes may be ameliorated through reuse of waters needed by the process. The economics of reuse depend on the volume of waste effluent, the cost of available fresh water as compared to the cost of treatment, and the cost of possible damage suits from users of the polluted effluent. Reuse has proven effective in steam electric power plants. The steel making industry and the auto industry improve the quality of the effluent from their phosphate coating operations by recovering phosphates for reuse. Other solvents in the effluent were also reclaimed as a result of careful extraction studies. The minimization of this type of pollution is reducing the phosphates that contribute to algae growth as well as reducing other minerals toxic to aquatic life.

An approach to solid and liquid waste disposal that offers the promise of pollution control is the Boule three stage incinerator which can handle solids, gaseous wastes and liquids. When combined with a scrubber, the method reduces solids to a sterile ash and provides total waste disposal for pollution control.

Recent studies show that disposal of solid waste in the ocean, ostensibly to avoid the pollution of land and fresh water sources, has caused the destruction of all plant and animal life in the disposal area. In 1968, 48 million tons of waste were dumped in the ocean waters off the coast of the U. S. It is recommended that future dumping be carefully controlled and limited to inert materials unless adequate containerization is used. It may be permitted only in areas over one mile deep and 25 miles from the nearest land.

A serious water pollution problem is created in and around abandoned mine shafts where acidic effluents from solid wastes left over from the mining operation drain into streams and lakes. The problem is acute and recent anti-pollution laws are focusing attention and research effort upon it. The use of lime, limestone, or a combination of both is coming into consideration again. Lime neutralization is costly, requires long settling times, and produces high calcium sulphate hardness in the effluent. Acid inhibiting bacteria, flash-distillation, and an experimental electro-chemical method are also under study. Prevention of the drainage is, of course, another approach. Uniroyal is experimenting with a latex barrier which solidifies upon contact with an acid soil; the object is to reduce the amount of water available for drainage. Tyco Labs is using sodium silicate on coal-tailing refuse piles to create a gel-like iron silicate to prevent water from entering and to precipitate iron from water leaving the piles.

Streams neutralized by limestone from the acidic drainage water still require the removal of iron to meet pollution standards. Several ways are used to accomplish this including aeration followed by filtration, or settling and precipitation. Brookhaven Treatment Laboratory is proposing the use of ozone to oxidize ferrous oxide. At Phillipsburg, Pennsylvania, a large scale demonstration plant is under construction for the ion exchange treatment of acid mine drainage. Activated carbon catalyses the air oxidation of the iron oxides and may be reused repeatedly. Its incorporation into the acid mine water treatment process facilitates neutralization, lowers reagent costs, eliminates aeration equipment, and permits pH control.

## D. Land and Soil Pollution

Solid wastes, pesticides, and other contaminants are creating as many serious pollution problems for the land as those that have been recognized for the air and water. Millions of appliances and automobiles, untold quantities of trucks, buses, airplanes, boats, railroad cars, scrap metals, construction and demolition wastes, and millions of tons of mining waste have been disposed of in a haphazard fashion creating esthetic, health, and other problems across the land.

Residential waste is a serious problem and is produced at the rate of 185 million tons annually with a threefold increase expected in 20 years. A large proportion may be salvageable as this waste contains roughly 30% paper and fiber, 13% glass, 13% metals, 4% plastic, and the balance miscellaneous. One major source of waste is in comsumer packaging which produces approximately one pound of waste per person per day. Most packaging materials become waste as soon as the contents are used, and the advent of the discardable container whether glass, or metal has only added to the problem. By 1976, it is estimated that the use of non-returnable beverage containers will double from 30.5 billion to 62.8 billion units. Unfortunately consumers appear to prefer the non-returnable containers. Predictions for paper use show the same trend because use in 1980 will be 39 million tons or about twice the 1968 use of 21 million tons, with the 1980 figure doubled by the year 2000. By the year 2000 also, virgin wood supplies may be inadequate to meet the demand.

Plastic coatings used for milk container paper stock, or plastics used for bottles and other stock are not degradable, add to the burden of solid waste disposal, and their usage is estimated to triple in 10 years.

Insecticides and herbicides which may persist in the soil for many years pollute the soil and have side effects about which little is known. One such side effect involves the so-called soil animals - mites, pauroropods, springtails, and larvae - whose population may be drastically decreased by persistent insecticides. Fumigants sterilize the soil to a limited depth. Although the soil is recolonized in a short time, its return to a stable concentration and distribution of soil animals may take several years.

Earth worms have been shown to be relatively insensitive to most insecticides. Chlorodane, heptachlor, phorate, and carbaryl deplete earthworm populations, and aldrins dieldrin, heptachlor, and DDT exist in the bodies of earthworms in concentrations up to ten times the values in the surrounding soils. The position of worms on a lower limb of the food chain may result in undesirable levels of those substances in higher animals. Various experiments have been conducted to study the effects of chemical pollutants on soil animals; no general patterns emerge; in fact, some soil animals show population explosions as others are wiped out but gradually the balance returns to normal. The major results of the experiments indicate that the most drastic effects of the pollutants disappear in a few years and that even the more persistent insecticides gradually degrade.

## E. Reclamation and New Trends

Traditionally solid waste has been disposed of through a landfill operation of some kind. With volumes of waste increasing, suitable sites for landfill disappearing, the rise in cost of this type of disposal, the exploding population and its concentration in urban areas, the indications are that solid waste disposal will continue to create difficult problems whose solution will not yield to money alone. Reclamation of solid waste and sale of the by-products is a possible future trend but cost competition is very severe at present.

Composting of organic solid wastes is a method of disposal and partial reclamation that has been available for many years, but it must be promoted as a waste disposal method rather than as a profit making business. It will also require reeducation for acceptance. The operation combines two distinct treatment phases: mechanical and biological. Mechanically the waste is sorted, screened, crushed, and glass eliminated. Biologically aerobic or anaerobic decomposition takes place producing a final product similar to humus. The City of Houston, Texas, maintained a successful composting operation which treated 400 tons of refuse and 120,000 gallons of activated sludge daily producing 250 tons of marketable organic compost daily. (This plant has been closed due to poor markets for the compost.) In other applications, leaves and cannery waste are disposed of by composting after receiving a special treatment.

Another attempt to reduce the waste disposal problem is being made through pulverizing the waste. Pulverization is helpful in composting and in landfill operations because it decomposes more rapidly, has less bulk, and is believed to be more resistant to rat colonies, to reduce fire risk and to eliminate insect breeding grounds. Special attention is being paid to the disposal of tree bark. In Sweden, bark is used as an ingredient in building blocks; Rugonier is extracting silvi-chemicals from bark producing compounds that form impermeable gels for growing, and chelating agents for soil minerals. Other uses for processed bark arise in horticulture where it may be used as a growing media, mulch, a soil amendment, or a garden cover. Wood chips are satisfactory as a poultry litter, as well. Generally, the bark accumulates at sawmills and is disposed of by burning or dumping.

Current research at Louisiana State University and other laboratories is attempting to convert cellulosic wastes into protein for human consumption.

Results of some of this research are presented in several tables in the survey review. Present processes for the production of these single cell proteins are not competitive with soybean protein in cost.

Pollution caused by soil erosion is being solved in a number of ways. Use of sewage sludge waste, fly ash, and pulpmill waste as soil stabilizers tends to solve two pollution problems simultaneously. Other erosion solutions that have been proposed that use polyethylene film as a mulch for agricultural crops, and soil stabilizers created from a synthetic rubber spray, formaldhyde resins, an asphalt layer below the surface, and other similar products.

Acid mine drainage, as the result of bacterial action, occurs because certain bacteria use the ions in the water that has percolated through mine waste for their metabolism process and the acid mine waste is given off in the process. There is no single group of microorganisms associated with the phenomena. To halt acid mine drainage, either the leaching water must be cut off or the growth of bacteria in the iron enriched water prevented.

The problem of the disposal of solid mineral wastes left from all mining operations is comparable to acid mine drainage. It may be necessary to convert it to a stabilized state or to usable material. The volumes involved with typical wastes are immense and represent the discard from selective mining or the residue of smelting or milling operations. The fine particles may be stabilized through physical, chemical or vegetative methods. Physically they may be covered with coarse slag, concrete, or soil. Chemicals may be used to bind the particles together, but stabilization through vegetation is more promising. (Extensive tests have been performed on all methods.) Some of the waste is suitable for fill or as raw material for construction products.

Flue dust containing zinc, lead, iron, and other minerals has been successfully treated to remove the zinc and lead, through the use of fuming and leaching. Automobile scrap placed in a rotating tumbler removed copper from the leach solution by cementation.

Phosphate rock converted to fertilizers and phosphoric acid produce wastes consisting of slimes, impure gypsum, ferrophorphorus and calcium silicate slag all of which have very limited use as fertilizer, soil addititive, roadfill, or similar uses. The ferrophorphorus is a raw material from which vanadium may be recovered and the Bureau of Mines is working on an experimental process which produces super - phosphate fertilizer and nickel as by-products.

Copper mill tailings from six western producers were treated by flotation to recover sulphide minerals. Fluidized bed roasting when tested burned off sulfur or its oxides; 92% of the copper in the tailings were extracted. Tailings have also been used successfully in a feasibility study to produce building brick.

Radioactive wastes and wastes from other industrial processes may be incorporated in cheap, impervious media such as asphalt or plastice to prevent leaching, odors, or dispersion by the wind. The waste asphalt or plastic product may be placed in rural landfills where cover would render the area fit for agricultural use or dumped into the ocean or other body of water without pollution since they are water insoluble. Preferrably they would be used with other insoluble aggregates such as limestone or sand for roads, roofing, or building blocks. The radioactive wastes used in these applications must necessarily contain only trace amounts of radio-nuclides. A number of tables in the survey report present types of waste materials acceptable for disposal by incorporation in asphalt or plastics.

Cooling water required by nuclear power stations dissipates large amounts of heat to the environment. These heat sinks are suspected of modifying local weather. One suggestion for heat dissipation involves the construction of large cooling canals which would use the heat to warm adjacent agricultural land to enhance crop production. These suggestions apply equally well to the use of existing irrigation systems to supply cooling waters to large power plants. Planning for the use of these waters must be undertaken on the same scale as the volumes of water concerned-quantities in the order of 1000 cfs per power plant and should provide for multipurpose use for the water.

High-temperature (2800°F) incineration, investigated at the Illinois Institute of Technology Research Institute, offers a chance to change solid waste into high-value products instead of a slag worth less than $2 per ton. The process yields a molten metal/glass melt which has the capability of being converted to filter pads, abrasives, iron castings, insulation, sewer pipe, etc. High-temperature incineration reduces solid wastes by 95%; this is another factor in its favor.

The much maligned "junk" dealer is still a potent force in solid waste disposal, although he deals primarily with scrap iron. In 1966, the approximately 1200 dealers in the U. S. processed 83,000,000 tons of scrap iron. The reduction in the amount of scrap used in the steel industry is having a repercussion in the scrap industry.

## F. Legislation

Legislation proposed or in committee on the Federal level at the time the survey review was prepared is outlined.

Public Law 91-127 which represented the Department of Agriculture's appropriation included $131 million for research part of which is to be used to study management of animal wastes.

One of the most important and far reaching pieces of environmental legislation is the Natural Environmental Policy Act of 1969 - Public Law 91-190 which includes the following:

(1) A natural policy and goals statement;

(2) Authorization for all federal agencies to administer existing laws, regulations and policies to conform to the act;

(3) Establishment of a three member Council of Environmental Quality.

In 1970, Public Law 91-512, the Resource Recovery Act was enacted into law, and provided federal assistance for resource recovery and solid waste disposal programs. The Law spells out in detail how the assistance shall be provided to meet the goals and objectives of recovery and disposal.

## G. Bibliography

The survey review was written on the basis of the data and information obtained from 116 references listed in the bibliography at the end of the survey review.

# CHAPTER 8. "MODIFICATIONS OF SOLVAY PROCESS SOLID WASTE DISPOSAL," M. S. THESIS, R. J. NORWOOD (JUNE 1971)

## A. Introduction

This investigation covers a continuation of the work reported by Boecher, *The Rehabilitation of the Solvay Process Waste Beds.* (See Chapter 6.) As this work is a continuation, some areas covered in detail in the previous reported study will only be covered briefly here.

Boecher, in his study, concluded that:

(a) The waste can be leached and drained if adequate drainage is supplied in the form of sand drains and drainage tiles.

(b) Vegetation can be supported on top soil over the waste beds if proper drainage is supplied and maintained.

(c) The soluble portion of the waste can be removed if proper drainage for the water is made available and the surface of the waste is disturbed periodically.

(d) The waste is a soft, sensitive material resembling a clay that can never be expected so support large structures.

(e) The rehabilitation of this waste can be accomplished to support parks, golf courses, and other low-load bearing facilities if proper drainage facilities are furnished and maintained.

Present waste beds are surrounded by dikes which have drainage ditches on the top. These empty the wastes onto the beds. This process results in heavier particles settling out rapidly near the dikes creating a beach; the finer particles and water pond in the middle of the beds; and the solution is drained off through a vertical pipe near the center of the beds. This solution is then emptied into a nearby creek. When the particles fill up to near the top of the dike, the dam is heightened and moved in on the bed on the area which was previously beach. This process is continued in increments of 4 to 5 feet until the state allowable total height of 60 feet is reached.

This study concerned itself with a depth study of the two initial conclusions of Boecher. "Proper drainage" was installed in a series of simulated laboratory waste beds. These were allowed to drain and leach. Drained material was examined as to the effects in growth of vegetation under six types of drainage conditions.

## B. Background of Solvay Process

The Solvay Process is known technically as the ammonia-soda process. Soda ash thus produced is used in the manufacture of glass, detergents, soaps, pulp and paper, textiles, water softeners, caustic soda, sodium phosphates, and sodium bicarbonate.

Mining of soda began about 90 years ago and has become more important in the last five years. Mined soda ash now comprises almost 36 per cent of the soda used in the United States. Mining of soda has become more important due to environmental concern. The control of chlorides in the effluents from manufacture of synthetic soda ash is more costly and thus the synthetic process is losing its economical advantage.

The Solvay Process is not simple to operate commercially; it can be carried on only through large scale operations. Tremendous amounts of salt, limestone, and fuel among others are necessary as raw materials. For economic convenience plants are located near one or more of these raw materials.

The Solvay Process may use either rock-salt or sea brines for the required salt solutions. Rock-salt brines are usually formed by extracting the salt with water; in some cases natural brines are formed by underground water flowing through the deposits. Sea brines contain many impurities of which some can be removed by crystallization (calcium and magnesium salts). Natural or artificial brine from rock-salt deposits contain as a principle impurity calcium sulfate (gypsum). Rock-salt as a raw material for the Solvay Process is superior to sea salt.

Impurities of calcium carbonate, magnesium carbonate and hydroxide, and iron hydroxide are precipitated in vats. The clarified brine flows to the strong ammonia or first absorber where it takes on the necessary amount of ammonia. The ammoniation liberates much heat from the dissolving of $NH_3$ gas. The solution at this point contains 83 grams of $NH_3$ and 260 grams of NaCl per liter. Carbon dioxide is absorbed with the ammonia. The brine is then settled, cooled at 25°C., and pumped to carbonating towers. Carbon dioxide is obtained along with calcium oxide by calcining limestone mixed with coke. Some additional carbon dioxide is yielded from the burning of the coke necessary to supply the heat required to decompose the limestone. The partly carbonated and warm brine is fed to "making" towers by carbon dioxide lifts. The first carbonating tower reactions form ammonium bicarbonate in solution. In the second tower sodium bicarbonate is precipitated after the ammonium bicarbonate reacts with salt.

The drying (calcination) of sodium bicarbonate is one of the most difficult steps in the manufacture of soda ash. Washed and moist sodium bicarbonate is charged into a furnace by feed tables which are gas sealed. Problems arise because moist sodium bicarbonate has a tendency to cake and form non-conducting scale on the steel shell of the calciner.

The hot soda ash from the calciner passes through a rotary cooler and is screened in a vibrating screeen of 8 to 12 mesh. The ash is then packed in bags for sale. Ash for the glass industry is coarser and denser. It is advantageous for the glass industry, even though it costs more, because less dusting results.

For economic operation of the Solvay process, the ammonia must be recovered. For any given time the value of the ammonia in the system is several times the value of the soda ash produced.

### C. Background Review of Slurries

Congress by the Solid Waste Disposal Act of 1965 delegated to the U. S. Bureau of Mines responsibility to conduct research designed to prevent air and water pollution from accumulations of solid mineral waste. The Bureau brochure *Wealth Out of Waste* states that in 1965 the accumulated tonnage of waste from the processing of minerals and fuels amounted to 1,122 million tons covering approximately 2 million acres and that over a billion tons of such mineral processing wastes are produced in this country each year! Of this total, 40 per cent is fine-sized material. Stabilization of these wastes to prevent air and water pollution and, concurrently, preserve the contained values for possible later utilization is a challenging task.

Stabilization of fines from flotation mill and leach plants present varying problems of varying magnitudes. Wastes near populated areas present the most problems. Fine wastes that dry can present air pollution problems while slurries that don't lose their moisture are unstable in other ways.

Mine wastes fall into two general classifications: coarse (over 1 mm in size) and fine (smaller than 1 mm). The manner of disposal of the two is vastly different. Coarse materials are usually piled while fines are sluiced as a slurry to settling ponds. After the water is drained off the partially dry material is stored for later use. A suggested solution for the mine waste problem is a more complete and more economic utilization of the waste portions resulting from production and processing of minerals.

### (a) Design of Tailing Ponds

It is apparent from literature research that industry has conducted, or sponsored, few soil mechanics studies on tailing disposal system. Companies have relied heavily on consultants who design dams which are traditional for holding water. In the past operating firms have been concerned mostly with getting out and disposing of tailing wastes as simply and easily as possible. This is undoubtedly the case with small firms as well as with larger firms.

The same assumptions and techniques ordinarily used in water retaining dams are used in tailing disposal systems. After considerable exploration it is clear that many assumptions are not accurate. Tailings, produced by mill crushing, screening and sizing have different characteristics from earth.

### (b) Aluminum Ore Processing Wastes

Bauxite ores are mined in Arkansas or imported from the Caribbean deposits. These ores are processed in at least seven plants in the south located in the states of: Arkansas, Alabama, Louisiana and Texas. The ore is extracted usually by the classical Bayer process; in two plants a combination Bayer/Sinter Process is used for higher recovery of soda and alumina from high silica domestic ores. In spite of many past and present attempts to extract aluminum from common silicate ores, bauxite remains the most economic of alumina feed materials for reduction to aluminum metal.

Solid wastes from the Bayer process are discharged into drying ponds as a 20% slurry. Deposited wastes are then called "red muds." Red muds may be further broken down into "black sand" which is 8 to 18 per cent by weight. "Brown muds" are the waste product of the combinations process.

Total solid waste from alumina processing industry is above 5 million tons per year. The amount of bauxite mined is above 10 million tons per year. Estimations of previously deposited alumina processing tailings is put at 100 million tons.

Considerable effort has been expended toward finding uses for "red muds". These fall into:

(1) Recovery of major constituents;
(2) Recovery of by-products;
(3) Direct uses; and,
(4) Incorporation into products.

(c) Phosphate Waste

The primary material for phosphorous production is phosphate rock. Phosphate is mined mainly in Florida, North Carolina, Tennessee, Idaho and Montana. Florida produces about 70% of the phosphate produced in the United States in the 20 by 30 mile Bone Valley District.

The phosphate ore is composed of approximately 1/3 sand, 1/3 clay, and 1/3 phosphate ore. The clay part when combined with water in processing produces the phosphate "slime." Significantly, 30 to 40% of the phosphate values are lost to slimes. Slimes are sttled as tailings and water siphoned off and reused.

The biggest problem in phosphate mining is the disposal of the slime which is one-half of plant wastes and one-third of the total matrix mined. For each cubic foot of matrix mined, 1.2 to 1.5 cubic feet of waste results (semi-dried slime). The slimes contain a very high percentage of water even after years of settling. The slimes are 4 to 5% solids as they leave the plant and rapidly settle to 10 to 15% in settling ponds. After years of settling, the slimes still only reach 25 to 30% solids. This makes former settling ponds hard to reclaim as land for any useful purpose.

The phosphate slime problem has been approached from the following conceptual efforts:

(1) To attempt to reduce waste disposal costs and attendant potential sources of water pollution;

(2) To speed up the drying process to facilitate land reclamation;

(3) To conserve natural resources of water and minerals; and,

(4) To develop by-products using phosphate slimes.

There seem to be major obstacles in the way of successful utilization of phosphate slimes. These are:

(1) The low solids in the slimes as discharged from plant processes;

(2) The slow settling of solid material;

(3) The high water content of settled slimes; and,

(4) The extreme fineness and colloidal properties of the mineral constituents.

Impounding slimes in settling ponds is advantageous over flooding of nearby lands so that river pollution is prevented. Mined out areas are very suitable for depositing slimes. The cost of building retaining dams around the mined out areas is a problem to the industry. There are other disadvantages to disposing of phosphate slimes in settling ponds:

(1) The ever-present possibility of accidental release of polluting slimes;

(2) The high construction and maintenance costs of the impoundments; and,

(3) The loss to the slime of large volumes of water as well as one-third of the phosphate value.

The literature shows one excellent example of water pollution from phosphorous plant effluents in Newfoundland. In December, 1968, it became evident that phosphorous was getting into the ocean as shown by the fish kill that resulted in early 1969. By May, the plant voluntarily shut down because of public pressure brought about by possible injury to the gigantic fishing industry. Now the insoluble phosphorous will have to be dredged at great expense from the bottom of the harbor.

(d) Copper Ore Tailings

Over 90% of the copper mined in the United States is mined in five western states. Most of the rest comes from Tennessee and Michigan. Arizona produces 50% of the United States production of copper with Utah ranking second.

Copper is found in a variety of host rocks and deposits. Porphyry deposits (deposits characterized by huge size, uniform dissemination, and low average copper content) contain most of the world's reserves. Copper ore is concentrated by flotation. The tailings are concentrated to about 35% solids and discharged to ponds as slurries. The effluent pH varies from 4 to 10. Besides the large volumes, copper slurries are a problem in another way. When dried the tailings are easily blown around by the wind and cause dusting. Considerable effort has been put forth toward stabilization of pond surface with chemicals and vegetation.

Bingham of the White Pine Copper Company (White Pine, Michigan) in order to illustrate the scope of their waste disposal problem stated: "Our tailing dam is the largest man made structure in all the 350 mile-long Upper Penninsula of Michigan and it took just fourteen years to fill it up. A new dam under construction will have more capacity." He also complains of multimillion dollar investment for these dams. "The problem of waste disposal is two-fold; first, try to find a use for the waste -- that is, convert it to a by-product; and failing this; dispose of it as efficiently, as safely, and as attractively as possible."

### (e) Iron Ore Tailings

Taconite is located throughout the world but particularly in the Mesabi Range in Minnesota. A large portion of the world's iron ore deposits are taconite. The ore is composed of approximately 73% other materials. Production of iron also produces 60 million long tons of tailings per year, which is two-thirds the amount mined. Coarse and fine tailings are produced at the concentrator where 90% of the ore is ground to 325 mesh. The coarse tailings are used to build earthen dikes or retaining walls to hold and dewater slurries. A survey (1964) of the principal accumulations of iron ore tailings showed 553 million tons accumulated with 427 million tons in Minnesota and Michigan.

Overflows and fines usually contain the following materials: hematite, geothite, quartz, chert, clay, plus small quantities of talcose silicates, iron silicates, iron carbonate (siderite) and gangue carbonates. The material is usually smaller than 65 mesh with a high percentage of earthy and argillaceous components which are called mineral slime. The iron content may range from 10 to 40 per cent.

(f) Lead-zinc Ore Tailings

Lead and zinc ores are mined in more than 250 operations throughout the United States. Most ore is mined in about 40 mines. Lead and zinc deposits are found in carbonate rocks mostly limestone and dolomitic limestone. Most ores range from 2 to 9% in the metal content, the average being 4% metallic content.

Missouri produces 5.5 million short tons of lead ore yearly. This amount produces 5 million tons of tailings. Tennessee is the leading producer of zinc with more than 20% of the national production. Its dolomitic limestone tailings have principal uses as agriculture lime with a lime equivalent of 90, road stone and ballast, asphalt filler, and No. 2 mortar sand (98% - 19 mesh and 13.5% - 200 mesh). Dried fines from slime ponds tend to dust during windy weather, water and soil being placed over the slime to minimize this effect.

(g) Coal Tailings

Overlooked in literature due to the large problems of acid mine drainage and mountainous sized slag heaps is the disposal of coal tailings. These tailings are slurried by the flotation process removing wastes from coal. The slurries are 4% solids and seldom seem to the casual observer to be anywhere near the volume of the slag heaps. Slurries are dewatered in ponds usually located between two slag piles. These slurries readily lose their moisture and during high winds will blow into the air and deposit a thick black dust on near areas. For this reason coal tailing ponds are seldom located near a village but are adjacent to the coal processing plant.

### (h) Stabilization of Slurry Wastes

Stabilization of fine sized slurry wastes is necessary to prevent air and water pollution and at the same time rehabilitate wastes as soil and preserve land value. Fine sized wastes are estimated to be more than 400 thousand tons per year. Several methods of stabilization for relatively fine wastes have been tried. These include physical, chemical and vegetative stabilization with many combinations thereof.

Physical stabilization is perhaps the simplest method to prevent air and water pollution. The most common method here is sprinkling water on the waste. The next most common method is spreading rock and soil over fine material; this method may be advantageous as plant life may grow on replaced topsoil. Topsoil, however, is not always available. Other methods of physical stabilization include: (1) Use of bark covering; (2) Harrowing of straw into the top few inches of tailings; (3) Placement of windbreaks; and, (4) Concrete or asphalt covering.

Chemical stabilization involves reacting some chemical with the waste to form an air and water-resistant crust or layer. Mill tailings often cause complicated reactions to form crusts as the surfaces are seldom homogeneous. The permeability, reactivity, pH, and salt content of the surfaces usually vary considerably.

Vegetative stabilization involves not only initiation but also perpetuation of vegetation on fine or coarse wastes. There are several adverse factors which have to be over come: (1) Lack of necessary plant nutrients; (2) Excessive salts and heavy metals; (3) Composition of unconsolidated sands that during blowing cause sandblasting of young plants; and, (4) Lack of normal microbial populations. The sloping sides of waste piles cause varying amounts of light exposure which may be harmful to growth. Many solid wastes are light in color and reflect light. Dean and Havens stated that: "Ideally, vegetative stability should produce a self-perpetuating plant cover directly or else faster entrapment and germination of native plant seeds which will form a self-regenerating community. If the area were not cropped or grazed, only an initial fertilization should be required because the essential nutrients would be largely cycled in place."

Salts are one of the major deterrents to growth in fine wastes. A study with wastes from Kennecott's Utah Copper Division showed: (1) Salt concentration had more effect than copper concentration; (2) Osmotic concentration of salts seemed to be the determining factor rather than the type of salt; (3) Osmotic gradient between plant fluids and the environment around the plant roots dehydrated the plants; and, (4) Further tests indicated that osmotic pressures did not hinder initial germination but further growth was inhibited unless the salts were leached from the wastes.

## D. Experimental

### (a) Procedure

The primary purpose of this study was to examine Solvay Process wastes deposited under different methods of drainage. Six basins were constructed 3 ft. wide, by 4 ft. long, and 4 ft. in depth. In three of the basins, sand and rock underdrains were installed; three of the basins had no underdrainage. The underdrainage consisted of 4 inches in depth of pea-sized stone with 3 inches of fine sand placed on top of the stone.

The basins were set up as follows:

(1) Basin Number one and three had sand and gravel underdrains and were loaded with waste from Solvay Process at a uniform rate.

(2) Basin Number two and Number five had no underdrainage but a provision was made to drain off water after waste had settled.

(3) Basin Number four was equipped similarly to one and three but Solvay waste was mixed with partially digested sewage sludge (four volumes of waste to one of sewage.)

(4) Basin Number six had a vertical sand drain. All the water had to flow through the sand drain and out the bottom of the bed.

Waste was trucked in two hundred gallon plastic barrels from the Industrial Chemical Division, Allied Chemical Corporation (Solvay, New York) to the loading platform where the basins were located. Trips were made once a week; a total of three hundred gallons was hauled each time, furnishing approximately 50 gallons of waste to be applied to each bed. This quantity produced a depth of 1/2 foot of liquid waste, in each basin.

Waste effluent samples were collected and analyzed for total solids, suspended solids, alkalinity, and pH. Their results were recorded. Samples from beds with no drainage were collected after 6 to 8 hours of settling time had elapsed. Samples of sand drained effluent were collected as the leachate water came through. The total time for the liquid portion to drain through the total waste was recorded as was the depth of the bed. Permeability tests were run in the laboratory with fresh waste.

The secondary purpose was to determine whether the Solvay waste was capable of supporting growth. Comparisons between drained and undrained sludges were carried out. One half to one inch of fine sand was placed on a bed with drainage and a bed without underdrainage. This sand was to act as a capillary boundary for the salt solution. A four inch layer of dark topsoil was then added to all beds except the bed with vertical sand drainage after 2 months settling starting with:

(1) Waste with underdrainage, 1/2 to 1" of fine sand, and 4" topsoil;

(2) Waste with no underdrainage, 1/2 to 1" of fine sand, and 4" topsoil;

(3) Waste with underdrainage, no sand layer and 4" topsoil;

(4) Waste with sewage sludge mixed and 4" topsoil;

(5) Waste with no underdrainage, no fine sand, and 4" topsoil; and,

(6) Waste and vertical sand drainage.

The beds were then seeded with grass with the following specifications and watered regularly:

| | | |
|---|---|---|
| 61.57% | Kentucky Bluegrass | - 80% germination |
| 35.23% | Creeping Red Fescue | - 80% germination |
| 10.22% | Chewing Fescue | - 85% germination |
| 2.89% | Inert Matter | |
| 0.09% | Weeds | |

Temperature was controlled at 70-74 degrees Fahrenheit, using electric heaters. Light was supplied by Gro-Lux light bulbs, ten and one half hours per day.

(b) Data

The following numbered and named tables from the reference thesis present the collected data:

Table IX, Depth of Wet Sludge, shows the depth of sludge deposited with 50 gallons of liquid slurry.

Table X, Time of Run, is the time required for the liquid to seep through settled waste.

Table XI, Total Solids, is a total solid analysis of effluent from each bed in ppm.

Table XII, Suspended Solids, is a suspended solids analysis of the effluent from each bed in ppm.

Table XIII, Alkalinity, is an analysis of total alkalinity of the effluent from each bed in ppm.

Table XIV, pH, is the pH of effluent samples from each bed.

Table XV, Summary, is a summary of Tables XI through XIV.

Tables XI - XIV, show representative values (usually mean) of the tests shown in these Tables.

Table XVI, Percent Removals, is based on Table XV, showing relative per cent removals of contaminants.

Table XVII, Moisture Contents, is a total solids determination on deposited waste, resulting in Water/Solid ratio. This ratio is used to determine relative reductions in volume between waste with and without sand underdrainage.

Table XVIII, Permeability, uses the results from Tables IX and X to determine permeability.

## E. Discussion of Results

Before any conclusions can be drawn, it is necessary to explain the variation in the concentration of the raw waste samples. The raw wastes varied from 10.1 to 21.5% in total solids. It is felt that the lower value is probably closer to the true value. The samples changed in composition for at least two reasons. First, there were relatively low amounts of cinders in the waste because cinders clogged a valve that made collection of the samples difficult and dangerous. Higher concentrations in the later samples were brought about by settling in the waste hoppers because the pump was turned off while the sampling line was tapped. High concentrations have no real effect on the experiments carried out in this study except in absolute values covering percentage removals; all data are thus comparative. Lack of cinders is more serious as in the present industrial waste beds the cinders settle out first near the dikes while the smaller fines make up a majority of the beds. The reported experiments were run with fines which cover the most critical case because fines do not give up water as easily as cinders and furnish a sensitive waste bed.

After only one loading the value of the vertical sand drain appeared questionable. Table IX showed no reduction in depth of wet sludge; depths were comparable to waste with no underdrainage. Table X showed 1.5 hours to drain with sand underdrainage and 3 days to drain through a vertical sand drain which is a fifty fold increase in time.

High order removals (95%$^+$) of suspended solids and alkalinity were shown by all methods of controlled drainage. These results were no doubt brought about by the alkalinity being highly concentrated in the suspended solids. Percentage removals of alkalinity and suspended solids varied by less than 3%. While beds with sand underdrainage removed a high degree of solids and alkalinity, beds with no underdrainage released about twice the amount of suspended solids and six times the amount of alkalinity into the effluent. With almost 100% removal of suspended solids only 33 to 34% removal of total dry solids was accomplished, indicating that the waste was 66 to 67% soluble. The pH of the effluent of the beds with sand underdrainage was somewhat lower than the bed with no underdrainage (10.2 versus 10.4).

The most important result obtained from physical data is the reduction in waste volume. After two weeks settling the basins with sand underdrainage had 41.5% less volume. Similar tests were made after four months; during two of these months the beds were covered with a 4 inch layer of topsoil. The sample with the sand underdrainage this time showed a 29.6% reduction in volume. These results indicate that considerable space could be saved by using sand underdrainage. The cost of underdrainage could be offset by savings in land dike construction. (Calculations are shown in the Appendix.) After the beds had been left inactive for a period of two months, an interesting observation was made. Beds with no underdrainage (including the bed with vertical sand drainage) contained 3/4 to 1" cracks into the waste. Beds with sand underdrainage had no large cracks and showed little evidence of any cracks. Cracking in this manner can be observed in other solid wastes with high liquid content, loss of liquid results in shrinking. Shrinking as cracking, results because undrained waste is less stable than drained waste.

Soluble materials are a major constituent of the Solvay Process wastes. These soluble materials can only leave the waste beds through seepage. Seepage is very slow but nevertheless occurs through dikes and there is some seepage through dikes and there is some seepage through the bottom of undrained beds. Seepage can be controlled with sand underdrainage; effluent caused by rain after the beds are inactive can be collected and as proposed, locally used in sewage tertiary treatment, rather than released directly to surface waters.

Tests run on the waste to find the coefficient of permeability were very consistent. Of five laboratory tests, the range was $3.66 \times 10^{-3}$ to $1.18 \times 10^{-3}$ cm/sec. while the mean was $1.52 \times 10^{-3}$ cm/sec. When the same test was run on the model waste beds the range was from $7.76 \times 10^{-3}$ cm/sec. while the mean was $2.33 \times 10^{-3}$ cm/sec. Using the mean of $1.52 \times 10^{-3}$ cm/sec. and

Q = KiA. 555 acres of sand underdrainage is required to drain 6.5 m.g.d. of liquid Solvay Process wastes. The 555 acres is an area requirement for a bed depth of 60 feet necessary to allow 6.5 m.g.d. seepage through the beds. While the acreage seems large the waste would be more compact, more concentrated and less toxic. An old waste column 60 feet high would be replaced by approximately 90 feet of waste due to higher concentration.

Experiments with grass seedlings were not as consistent as expected. Some growth occurred in the bed containing sewage sludge mixed with Solvay waste. The growth seemed to stop after the second watering perhaps caused by capillarity of dissolved salts. Contrary to expectations, grass also grew in a bed containing no underdrainage, however, this growth also seemed to terminate after the second watering. In both cases the grass didn't seem to die (turn brown); it remained green, but did not increase in length as grass in control areas did. No grass grew in the bed equipped with a vertical sand drain. Grass did not grow in beds with 1/2 to 1" sand used as a capillary boundary layer.

A large opposing factor to grass germination was the inability to control the temperature. Tests were run through the months of December, January and February. The outside temperature range was from 50° to -15° F. The enclosure was not well insulated and the inside temperature varied almost as much (at one time there was a power failure). Outside sunlight was near 20% of maximum and gave little help to the Gro-Lux lights.

Further simple experiments were set up as a supplement to grass growing to discover if leached waste could be less toxic than unleached waste. Two geraniums were set in waste, one with leached waste while in the second unleached waste was used. These geraniums were still rooted in their natural soil but received their water through waste. Neither plant was affected seriously but both plants wilted slightly near the tips of their leaves. Two other geraniums were tested with leached and unleached waste but this time the waste was applied at the base of the stem. In this case, both plants wilted slightly again but the plant with unleached waste more seriously. All four plants survived the previous experiments and recovered completely. Finally, one geranium was partially re-rooted in unleached soft fine waste. The geranium shriveled up, turned brown, and died.

## F. Conclusions

(1) Due to approximately a fifty fold increase in the amount of time required for liquid waste to seep through vertical sand drains, this method seems impractical.

(2) All methods of drainage remove a high order percentage of contaminants. Sand underdrainage allowed fewer contaminants to be discharged in the effluent.

(3) Significant waste volume reductions were realized by employing sand underdrainage. Volume reductions will lead to savings in land and dike costs.

(4) The volume reductions produce a more stable waste which means increased land value when the beds are completed.

(5) Unleached waste is toxic to geraniums and apparently to grass. Mixing sewage sludge in the top layers of the wastes may decrease this toxicity. Leached waste was somewhat less toxic.

## G. Recommendations

(1) Larger scale investigations with larger quantities and longer periods of time are needed to verify land requirements.

(2) Further growth studies on waste in place for a period of time are needed to determine if toxic salts continue to be a deterrent to growth.

(3) Further studies should include personnel familiar with soil mechanics to permit a basic approach to rehabilitation of old beds from the standpoint of compaction and settlement.

(4) Test plots of larger scale should be located on the currently used Solvay waste beds with and without sand drainage conformations. These would permit evaluation of growths of desirable vegetation under field conditions.

## H. References and Appendices

The reference thesis on which this chapter is based listed 20 pertinent references (pages 51 and 52). There are 20 tables covering direct collected, experimental and calculated data in the original presentation. Appendices A through C show calculations of permeability, volume reduction and flow.

The complete reference thesis is available through the Solid Waste Information Retrieval System (SWIRS) or on an Inter-Library Loan from Syracuse University.

# CHAPTER 9. "INHIBITION OF ACID MINE DRAINAGE BY MUNICIPAL SOLID WASTE EFFLUENTS" M.S. THESIS, CHRISTOPHER C. BIEMILLER (JUNE 1971)

## A. Introduction

### (a) Solid Wastes from Industry

Coal Mine operations in the U. S. Northeast destroy and depreciate land values by depositing wastes whose local presence may be a nuisance and a hazard and whose exposed pyritic surfaces extend deleterious effects for miles down receiving streams through the biologic and chemical phenomena of acid mine drainage. The existence of this huge land area touched by the effects of improper disposal of coal mine refuse is all the more unfortunate because of its location within recreational driving distance of the great eastern population corridor and inside the living perimeter of some of the Northeast States' major cities. The point sources of pollution are seemingly limitless, the responsible parties for legal action are elusive, and the practical technology to control and contain the problem is not adequate. Hodge estimated that $10 million worth of damage per year is caused by the direct effects of acid mine drainage. It is estimated that some 3 million tons of sulfuric acid annually enters the Ohio River Basin.

In the Appalachian area alone 10,000 miles of surface streams are polluted by acid mine drainage. 60% of the acid mine drainage in the U. S. is from abandoned surface and deep mine shafts. Pennsylvania reports that coping with abandoned mines alone may cost as much as $1 billion for corrective actions. The FWPCA estimates that the total costs of treatment of acids from active mines will require up to 95% treatment and cost $7 billion. What the final accounting will be cannot presently be determined! The past debt is outstanding from over one-half century of carelessness. The methods for treatment or abatement of currently produced acids are far from satisfactory.

(b) Solid Waste from Municipalities

By 1980 some 235 million people are expected to be generating 8 lbs./person/day of household solid wastes or more than 340 million tons per year. Overall the nation is generating today an estimated 10-11 pounds per person per day of household, commercial and industrial wastes or more than 400 million tons per year. About 90% of wastes collected go to some 13,000 land disposal sites, of which only about 6% are considered complete "sanitary" landfills.

The technology of landfill operations is such that one of the prime requirements for a satisfactory system is one involving hydraulic isolation of the fill from both ground and infiltrating waters. The reality of landfill operations more often than not dictates the use of lowlands not even acceptable for industrial development which, therefore, are relatively inexpensive. In many cases the refuse is actually deposited into water bearing areas creating noticeable odors as well as often overlooked water quality degradation.

This paper discusses several of the aspects of Acid Mine Drainage (AMD) and landfill leachates. In addition, an attempt was made to predict the interrelationships and possible benefits developing out of mutual waste depositions. Special interest is attached to any possible inhibitions or alterations in the production or composition of acid mine waters.

## B. Background

### (a) Coal Mine Refuse and Acid Mine Drainage (AMD)

#### (1) Scope - Sources - Dispositions

The scope of the solid waste problem in the anthracite and bituminous coal industries as reported indicates that for the year 1965, 102,600 thousand short tons of waste were produced from the production and preparation of 347,065 thousand short tons of marketable coal. The accumulated wastes in the coal industry from 1942 - 1965 are estimated to be 2,469 thousand short tons. The Appalachian Regional Commission reports that the twelve states that compose the Appalachian region produce over three quarters of the total U. S. coal production. Anthracite has been mined in Northeastern Pennsylvania for 150 years, with the production of more than 5 billion tons of marketable coal and 910 million cubic yards of surface refuse.

Coal mining is accomplished by methods classified as either strip, auger, highwall mining (all surface methods), or deep mining. Surface methods are often referred to as "strip" since a succession of narrow strips of overburden are removed from the above coal seam during the mining process. After the coal in the seam is removed, fresh overburden is deposited in its place from the stripping of the next row, filling in much of the older strip. The last strip that is mined will remain unfilled. Auger mining operations bore into the coal seam with giant augers that can penetrate from 100 - 200 feet. The holes are bored as closely as possible to one another, usually with only a separating pillar of a few inches to keep the seam from caving in. Auger mining is used when the coal seams outcrop but have too much overburden to allow stripping from above. In highwall mining, access to the coal is from the sides of the highwall, using underground mining equipment. The length of shafts in this case is variable, but they are again placed as close together as possible to insure thorough extraction of the coal. Bituminous coal is most frequently stripped, while anthracite is deep mined.

Extraction and preparation of the coal for various markets is the source of the solid waste and the secondary pollution effects caused by fires and acid mine drainage. As the coal is being removed from the seam, impurities in the coal bed and materials in the surrounding strata become mixed with the coal being brought to the surface for preparation. The bulk of unacceptable material mined is separated from the coal and deposited on nearby surface areas in the preceding strips, forming refuse banks. In preparation, coal and impurities are more thoroughly separated from one another to upgrade the marketable product. The extent of preparation varies from little to extensive separation of refuse from run-of-the-mill (ROM) product. The refuse material from preparation of the coal may be as much as 50% of the ROM, but generally runs less than that.

MacCartney and Whaite describe the methods of waste deposition in anthracite operations. The coarse refuse from the "breakers" is usually carried by vehicle to the deposit site. Coarse refuse deposits have been regulated by the Pennsylvania Department of Health since passage of the Air Pollution Control Act of 1960. The principal objective of the regulation is to minimize the possibility of ignition of the refuse, requiring it to be deposited in relatively thin layers, followed by good compaction. The regulation may control air pollution but this method of disposal may only exaggerate the problems of acid mine drainage. It is highly desirable that effective measures to insure pollution abatement from both sources be done at once. The silt wastes are carried away and collected in sedimentation ponds, or if of low quantity are released frequently into the streams. There are current Pennsylvania regulations regarding stream pollution by these silts. Other refuse and tunnel rock are often dumped directly near the mining operation and are usually small in volume reducing their nuisance value to that of a grading operation if they are inert.

MacCartney and Whaite report that the impurities in the mined materials which arrive at the processing plant are rock, slate (less than 40% fixed carbon) and "bone" (a high ash, medium carbon content material defined as any material containing between 40 - 70% fixed carbon). The rock, slate and bone must be removed from the ROM product in the breaker before the coal can be marketed. The relative percentages of each that are present in the ROM depend on the geology of the bed and surrounding beds, purity of seams, type and stage of mining (hand-mechanical, advance-retreat), and the use of explosives in breaking loose the coal from the faces. The breaker gets its name from the sizing of the ROM, during which process large impurities are removed, originally manually, but now by wet and dry techniques dependent on the specific gravity of the desired grade of coal. The breaker separates them by size and by specific gravity. The purity of silts separated in the breaker operations is often great enough to allow direct marketing after sedimentation, without further processing. Many of the coarse silt banks deposited early in the century contained as much as 30 - 75% acceptable grade coal and many of these coarse refuse deposits have been reprocessed for the coal. Refuse from modern breaker processing contains very little usable coal.

### (2) Fires and Pollution

MacCartney and Whaite report that the main thrust of regulations controlling solid coal mine waste disposal is directed towards abatement of fires and their inherent air pollution problems. Myers and others report that fires occur continuously throughout the areas covered by the solid coal refuse. Many research groups studying the beds for other purposes, comment on the presence of fires during their study. The materials in the refuse heaps, aside from the minerals previously mentioned, include such refuse as wood, machine parts, wire and electrical cables, paper and cloth, and grease and oils. The smoke from these "adulterants" only increases the pollution problems in the atmosphere caused by the high sulfur low carbon fossil fuels. Some fires are set deliberately to obtain "red dog" but Myers reports that most start spontaneously, either by brush fires or spontaneous combustion within the refuse heap. The proximity of these beds, and their attendant fires and air pollution to heavily populated areas discourages increased investment and development of the areas and creates a hazard with regard to the toxicity of many of the smokes produced from the smoldering heaps.

As with all problems inherent in mine waste control and regulation, the problems of ownership and responsibility for a problem such as extinguishing a fire are often impossible to establish. The Appalachian Regional Commission suggests a typical type of confusion that arises. A number of leased coal properties with multiple ownership is subjected to a joint mining and preparation operation by an owner of other coal lands and the refuse material is deposited upon surface owned by the operator of the mine and breaker. Dependent upon the nature of the agreement among the parties, the refuse may be the responsibility of the individual owners or of the owner of the mine and preparation plant.

Myers reports that active burning is generally most evident on the sides and the bottom of the slopes where the larger lumps of ignitable refuse accumulate during dumping. Many methods such as flooding, blanketing, slurry injection, compacting, "loading out" and sealing, have been tried to control the fires. Unless the temperature within the refuse heaps can be reduced below the kindling point, the potential risks of fires will be ever present. Over the past ten years, the Bureau of Mines has studied various methods for controlling refuse fires in mine wastes. The Bureau of Mines has sponsored studies on the permeability of coal piles to high volume air flows, the factors affecting the spontaneous combustion of coal wastes, the smothering of fires by capping with fine refuse, and the control of burning by water application both surface sprinkling and injection.

### (3) Acid Mine Drainage - Interphase Between Land and Water Pollution

The term "acid mine drainage" is applied to causes whose overall effect on water bodies is characterized by low pH (1 to 3), low alkalinities, "fish kills", sterility of stream beds and deposits of metal hydroxides. Acid mine drainage is as much a problem in solid waste management as it is in natural water resource conservation. Since it is the solid waste problem which initiates stream pollution, control and research should start at the source - solid waste management.

The scope of the effects of acid mine drainage is vast and complex. Water pollution by acid mine drainage has had ruinous effects which have limited severely or destroyed the productivity of large portions of the water resources of Appalachia and the Ohio River Basin. The increased costs to industry, required to pay for non-corrosive industrial water, inhibit industrial investment and expansion in already economically impoverished areas. The sterility of the natural resources deprives the highly populated and highly urbanized Northeast Corridor of badly needed recreational area.

Although acid mine drainage may occur as a result of lead, zinc, barite, and manganese mining operations, it is primarily a consequence of the anthracite and bituminous coal mining within the twelve Appalachian states and the Ohio River Basin. Sulfur and iron present during the formation of the coal seams combine to create the pyrites and marcasites that appear within the same strata. During mining operations, the ferrous sulfide materials are exposed to the air and water which through chemical and biological pathways produce the large quantities of sulfuric acid, dissolved solids, and precipitated slimes that are the marks of acid mine drainage. It has been variously estimated that some 3 million tons of sulfuric acid leached from active and abandoned mines and waste heaps run annually into the Ohio River Basin and its tributaries. The Ohio River is 981 miles long and drains an area of approximately 203,900 square miles. The Allegheny River from Pittsburgh to its headwaters is over 400 miles long. An estimated 7000 square miles of these lands are underlain by coal of which only a tenth has been mined. Only 10% of the acidity of the drainage waters is believed to come from any sources other than mine and mine waste drainage.

Many of the streams and rivers are navigable. The acid waters corrode navigational canal locks and dams, ships and barges, bridges and culverts and pipe lines and plumbing. In the non-navigable waters the acidity and hardness render the streams unfit for much of anything. Estimates as far back as 1937 were that acid mine drainage caused $10 million annually in chronic depreciation and deterioration of property in the Ohio River Basin alone. No estimates were made as to the losses due to degradation of the natural resources.

### (4) Chemical Parameters

Acid mine drainage waters are characterized by low pH and high sulfate and iron concentrations and the stream beds by the brilliant yellow iron precipitates called "yellow boy". Corbett and Growitz have reported analyses from five different coal mine drainage sources.

Pyrite and Marcasite are the two polymorphs of the mineral "iron disulfide", $FeS_2$. Pyrite is by far the most abundant in the Eastern U. S. Coal mine seams. Marcasite is the more reactive of the two. It is known that both of these minerals are sources for acid mine drainage. Clark's theory of the oxidation of the pyrites states that it is an electrochemical "redox" reaction, the insolubility of the pyrite making simple dissociation of the mineral improbable. The kinetic rate of analysis also shows that it is unlikely that the sulfate concentrations found in the coal mine drainage could come from any type of sulfide dissociation.

There are several suggested pyrite oxidizing agents: the ferric ion itself, dissolved oxygen, bacteria and water. Whatever the role of any of these is in the initiation step leading to acid mine drainage, it is clear that the rate limiting step in the preparation of acid mine drainage is the oxygenation of the iron ion. A study of anaerobic pyritic oxidation beneath the water table, although inconclusive, indicates that atleast theoretically water may supply the oxygen for the initiator step in the dissolution mechanism.

Oxidation of iron pyrites is a two step mechanism with several possible side reactions which depend on environmental conditions. The initiator step is a direct contact oxidation at the pyrite surface. This is shown to occur both by bacteria action and by direct oxygenation by dissolved oxygen. Agreement has not been reached as to which of these propagators is the more significant. It seems from the data available that the point is moot as either appears to be capable of initiating the mechanism.

Once the reaction has been initiated the next step involves the oxidation of the ferrous iron species, again either by direct oxygenation or by bacterial action. The subsequent ferric ion attacks the pyritic substrate in a "redox" reaction as a new initiator step thereby completing the propagating mechanism. The only continuous source of ferric ions for this reaction is through the reoxidation of ferrous ions. The absence of dissolved oxygen may not necessarily preclude these mechanisms. Dissolved oxygen cannot alone account for the production of acid mine waters. Barnes and Clark have shown that air saturated water, although capable of acid production at a pH 3.5 and Fe(II) concentrations of 10 mg./l. are incapable, when isolated from the atmosphere, of producing any greater concentrations, let alone the naturally occurring Fe(II) concentrations of up to 1000 mg./l and pH values of the magnitude of 2.5.

Silverman's examination of the oxygen uptake lag in acid pretreated pyrites versus non-acid treated pyrites shows that both the so-called direct and indirect mechanisms of pyritic oxidation can be involved. The lag is caused by the removal of soluble iron from the mineral. When the return of the curve again becomes parallel to the linear nontreated curve, it demonstrates that bacterial action can be affected on the substrate alone as well as with the dissolved iron portions. According to the indirect contact mechanism, ferric ions are the primary oxidant of the pyrites, oxidizing metal sulfides while being reduced in turn to the ferrous state. The bacteria then oxidize the ferrous ion to regenerate the primary oxidant.

### (5) Biologic Parameters of Acid Mine Drainage

Present action to limit acid mine drainage has been a policy of separating the pyritic material from the environment, by mine sealing and by back or land filling the surface "gob" material and diverting stream flows. These approaches seem to be the only currently acceptable methods for acid mine drainage abatement and coal mine solid waste disposal. There has been a great deal of research into the actual mechanisms by which these nuisances are formed. As yet, little of the published knowledge about the role of microorganisms and the inorganic kinetics has been directly applicable to pollution abatement.

In addition to the recognized role of bacteria in the cycling of carbon and nitrogen, bacteria have been known for some time to play a role in recycling of minerals. Heap leaching of low grade chalcopyritic ores and recovery of copper from the acid waters was practiced as far back as 1670 in Spain. It was not until the 1940's that the role of bacteria was recognized as a factor in the leaching of metals. In 1951, Thiobacillus ferrooxidans was isolated from the acid effluent of a West Virginia coal mine. Since then as many as nine different strains of bacteria have been identified as existing in acid waters associated with coal mine drainage. It is noted that in recent literature on the subject, these bacteria are loosely referred to as the *Thiobacillus ferrooxidans* group in keeping with the current lumping tendencies of contemporary taxonomists. It is reported by Pings that *Thiobacillus thiooxidans* although capable of oxidizing sulfur to sulfuric acid is unable to oxidize ferrous iron and metallic sulfides. *Thiobacillus ferrooxidans* is capable of oxidizing ferrous iron as well as the reduced states of sulfur such as thiosulfates, sulfur, and sulfides. This indicates that although there may be many bacteria associated with acid mine drainage, not all of them play essential roles.

### (6) Description of the Organisms

Of the various organisms that have been separated from waters associated with acid mine drainage only *Ferrobacillus ferroxidans* has been shown in the laboratory to be capable of the full range of acid production and oxidation of pyritic materials. Besides the several related bacteria of taxonomically related genera, only a few yeasts and fungi normally can survive in the harsh acid mineral inorganic environment. The organism as isolated is a short, gram negative rod requiring an acid environment of between pH 2.5 to 4.5, the presence of sulfate ions, and as an energy source the oxidation of ferrous to ferric iron. Several anions have proved to be inhibitors of the growth of the organisms. Pings reports that adaptability of the organism to cations is great. A pH value of 4.0 represents the upper limit for growth, but cell survival at a higher pH is reported. The growth of the bacteria in ferrous media without sulfur material did not contribute to any increase in acidity or sulfate concentration.

Lau, Shumake and Smith summarize the general understanding in the field of the role of microoganisms in acid mine drainage phenomena. The acidophilic iron oxidizing autotrophs can, under favorable conditions, increase the rate of pyrite oxidation by maintaining a high ferric-ferrous ratio in the solution surrounding the pyrite. The rate of increase is probably in accordance with established ferric ion oxidation kinetics. The rate of production of ferric ions by the cells is dependent on the total number of active cells in close enough proximity to the pyrite to allow diffusion of the ferric ion back to the pyrite surface. The organisms reach a limiting concentration of $10^8$ - $10^9$ cells/ml., and the degree of bacterial catalysis is thus dependent on the volume of water per unit of exposed pyrite. At 25° and under in the conditions of these experiments, the maximum rate of bacterial oxidation is equivalent to $5 \times 10^{-6}$ micrograms of $O_2$ per day per cell. Water-pyrite ratio is a factor not only in determining the total number of cells which can be attained in a given system, but will, together with the physical and mineral structure of the system, determine both oxygen and soluble iron diffusional rates and pH values in the aqueous phase. Additional work is necessary on the effects of pH and oxygen concentration on microbial activity. At present, the authors feel that there is sound evidence for the occurrence of significant bacterial catalysis of pyrite oxidation only in environments such as are found at the surface of refuse piles and spoil banks. Bacterial catalysis is less likely in underground environments.

### (7) Abatement of Acid Mine Drainage

It was not until the turn of the twentieth century that the heavy machinery necessary for large scale coal mining operations became available in the U.S.A. Previous to that time operations utilized pick and shovel methods on a small scale. In Indiana, commercial coal mining began as early as 1812. Studies conducted in 1913-1916 by the Stream Pollution Investigations Station, U. S. Public Health Service produced two pamphlets, No. 143 and No. 146 in 1923 on acid mine drainage. Acid mine drainage has occurred in this country naturally and has been observed for at least 250 years. Indeed it is the occurrence of natural acid waters that led to the discovery of some of the early mine sites.

The first comprehensive approach to the abatement of acid mine drainage occurred in the 1930's with a cooperative effort between the Federal and State governments via such relief administrations as the Works Progress Administration, Federal Emergency Relief Administration and Civil Works Administration. Neutralization and reclamation of by-products were the initial control programs at that time. Costs of treatment, with the high sludge volumes inherrent in the neutralization process, were, and still are drawbacks to any overall solution of the drainage problems by treatment. The lack of nearby markets for the sale of recovered by-products prohibited the economic feasibility of reclamation.

Approaches to solving the problem of acid mine drainage consist of various types of sealing methods of mines and refuse heaps and stream and runoff diversion and control. One method deprives the system of the needed oxygen and the other deprives the system of the required water. The third approach as mentioned earlier, has been to treat the problem after it has been created.

A study by Woodley and Moore describes the success that the State of Indiana has had in reclaiming wasted areas by reforestation and drainage planning. The drawback in revegetation as a reclamation method has always been that the time required for stabilization is excessive as compared to the high rates of wind and water erosion. The sterility of the topsoils by vertical leaching of solids toxic to plant life increases the problems. In Indiana, annual coal production has been 15 million tons; surface mining accounts for 72.5% of the coal production. Of the total 80,066 acres uncovered since 1914, a total of 76,413 have been reclaimed by reforestation, grass seeding, formation of lakes, and the establishment of private homesteads and recreational areas.

With regard to subsurface mines, the problems inherrent in sealing are obvious. Location of all the cracks and ventilation shafts is a monumental task for mines above the natural drainage level. Internal sealants have a drawback of losing effectiveness when fresh surfaces appear through "caveins" and slumping of walls. Mines beneath natural drainage levels will fill naturally if they are not isolated.

If preventive steps cannot be taken to inhibit the production of acid wastes, then treatment of some type is called for. One of the present problems in acid treatment processes is that although the immediate acidity is readily neutralized, the delayed acidity due to the redox changes in the metallic portions of the solution may not be effectively neutralized. It is these latter redox reactions that cause a large portion of the acidity of acid waters. Mihok reports on the catalytic oxidation of ferrous ions by activated charcoal. If systems can be devised whereby all the acidity is neutralized initially, then the system can at least be termed adequate.

There is growing acceptance of the idea that existing knowledge regarding the formation of acid waters from coal mine pyrite oxidation, and practical methods for the abatement of stream pollution from this acid drainage is sufficient to warrant positive programs for stream improvement in coal mining regions. Under current Pennsylvania Clean Streams Law (1967), discharges of acid mine drainage must have a pH between 6 and 9 with a maximum iron content of 7 ppm. It is estimated by Pollio and Kunin that at least 80 per cent of the mine waters in Pennsylvania will have to be treated to meet these standards. The FWPCA estimates that this treatment will have to remove 95% of the pollutants.

A test plot of copper mill tailings involving combined chemical and vegetative stabilization procedures is cited. A commercial resinous adhesive reagent was selected as the most economic soil stabilizer. Winter wheat was planted to provide a fast growing cover to prevent the chemical stabilizer from being washed away. Legumes were planted for their fertilizing properties and Siberian pea trees were selected for wind breaking properties. The primary objective of the project, to stabilize the waste heaps against wind and water erosion, seems to have been achieved at a cost of about half of what industry representatives had agreed was reasonable.

All major approaches to acid mine drainage (AMD) abatement are different approaches of sealing the pyritic material from one of the three mentioned parameters; water, oxygen, and bacteria. In addition, the natural aging of mines, slumping, caving-in, and fissuring make the physical task of maintaining seals non-economic. Despite the theoretical and physical considerations which foredoom the success of attempts to abate acid mine drainage by the exclusion of oxygen, a great amount of money and effort is being spent in this direction. Rice discusses the use of inert gasses such as nitrogen, methane (in high noncombustible concentrations), and exhaust gasses from power plants to prevent the formation of AMD. He details elaborate life support systems for use in active mines, and seals and pressure locks for both active and abandoned mines. He admits that to be effective, air must be excluded 100% of the time. He discusses mine "breathing". An increase in the barometric pressure of 0.2 inches of mercury requires 4000 ft.$^3$ of gas to be introduced into the mine per acre of area. This gas would have to be available continuously. This is not a realistic solution.

Shearer, Everson and Mausteller examined possible microbiologic inhibitors for use in acid mine drainage abatement. Their laboratory studies showed that acid production in piles of coal with water flowing through them can be reduced by factors as high as thirty to one, over periods of six months with only three applications of natural anti-bacterial agents found in the effluents of certain non-acidic mines. The actual agent involved is not specifically identified although it was reported not to be any bacteriaphage. The mechanism could be one of completion or simple parasitism by identified species of Caulobacter. Another suggested control might be brought about by the action of antibiotics produced by other organisms such as penicillin.

### (8) Effects of Dissolved Materials on Iron, Water and Acid Production:

Silverman and Lundgren report the following environmental conditions for bacterial growth; the optimal pH and temperature were 3.0 - 3.6 and 37°C.; no evidence of iron toxicity exists at concentrations as high as 500 micro-moles of iron III; phosphate moderately inhibits iron oxidation; citrate is strongly inhibitory; resting cells are unable to oxidize ammonia, thiosulfate, di and tetravalent manganese, cobalt or nickel; a slow but significant oxidation of elemental sulfur is observed. Razzell and Trussell report that low concentrations of thiosulfate inhibit sulfur and iron oxidation; that cations were generally innocuous; but that salts of halides and nitrates were inhibitory. Flourides and azides which might be expected to inhibit growth also prevented iron oxidation.

Robinson reports that although organic materials in ground waters do not interfere with the oxidation of ferrous iron, some organic extracts obtained from ground water can hold iron in a filterable condition in laboratory tests in alkaline conditions, and with sufficient excess iron all iron is retained by filtration indicating that organic materials probably create colloidal dispersions and not soluble chelates. It is hypothesized by Engelbrecht that interference with iron removal is caused by biologic activity supported by humic acids creating reducing conditions in a slime layer at the surface or within filters. This eliminates conditions favoring the reconversion of the iron to the soluble ferrous form.

Stumm and Morgan have stated that "colored waters have been collected from many parts of the country and without a single exception the color has been found to be a complex of iron". Unless iron is held in water solution either by chelation or in suspension by colloidal dispersion, conventional iron removal technology is sufficient to remove the iron to a satisfactory level with respect to drinking water standards.

Dugan and Lundgren suggest that the envelope surrounding the bacterium is filled with sulfate, phosphate, and iron ions, several ions thick, which allow electrons to migrate to various receptor sites. Organic compounds, if present, tend to line up or become attached to a layer surrounding the envelope and block further transport of sulfate and iron ions. This may explain the organisms inability to grow on most organic compounds. This concept is consistent with the observations of Remsen and Lundgren who found that cells in cultures in an iron sulfate medium are inhibited by most organic compounds, but can in time adapt to glucose as an energy source.

### (b) Municipal Solid Wastes and Sanitary Landfills

#### (1) General

Municipal solid waste disposal has been and still is a recognized source of great pollution. Historic disposal techniques have never been adequate for the problems. Either the air is fouled by incineration or anaerobic gas formation, or the downstream receiving waters are fouled by infiltrating water leachates. Air pollution technology has acted to improve the control of incineration but this has meant increased costs and hence encouraged the use of less costly and often less effective alternate means of disposal. It has been recognized that land disposal of refuse acts as a pollutor of water resources but the wide scope of the problem is only just being realized. Studies have defined some of the ways through which infiltrating water is contaminated as it passes through a refuse pile, whether it be compacted, loose, aerobic, or anaerobic. These studies have shown that the amount of dissolved material is very great.

### (2) Anaerobic Landfill

The American Chemical Society (1969) reports that of the 13,000 land disposal sites presently being used for the disposal of 90% of the refuse collected by public and private agencies in the U. S., only 6% are facilities that can be considered sanitary. The remaining 94% of the wastes that are disposed on land are therefore to be considered as creating a nuisance through burning, odors, gases, vector population support and water quality degradation. When dumps were located in remote areas pollution created by the effects of a badly run land disposal site on the population was minimal. With the spread of suburban development the remote areas became less distant and the undesirability of the areas became more and more significant. The sanitary landfill method of land refuse disposal was developed in the 1930's as an alternative to the prevalent open dump method (Salvato, Wilkie and Mead, 1970). This has since been approved by health authorities as an acceptable method of disposal on land. It is generally the least expensive and least restrictive with respect to waste acceptability and can be considered as a method of marginal land reclamation.

Decomposition and stabilization in a landfill is dependent on many factors such as refuse composition, compaction, moisture content, hydraulic gradients, and temperature. Only recently has there been any analysis of the parameters involved in the mechanism of landfill operation as a method of waste disposal. Landfills are basically of two kinds: anaerobic and aerobic. The anaerobic landfill is the natural consequence of a properly run site. Refuse is dumped by the collection vehicle at the site of the landfill and is spread in thin layers and compacted by a bulldozer doing the spreading before the next load is dumped. When about ten feet of refuse has been spread and compacted in this fashion, or at the end of the working day in the case of small operations, a six inch cover of compacted earth is applied to the lift daily. When the fill is brought to grade level a final cap of two to three feet of cover earth is applied. Air does not penetrate a well compacted landfill to any extent, and oxygen inside the fill is readily utilized by aerobic organisms as they decompose the organic matter. After the exhaustion of the free oxygen the continuing decomposition will be anaerobic and will normally only partially oxidize the materials and therefore only partially stabilize the fill.

Among the major products of anaerobic breakdown of refuse are methane, carbon dioxide, and organic chemicals with putrid odors and highly soluble solids with large oxygen demands. Most of the odor complaints pertaining to landfills can be traced to saturated fills and anaerobic conditions. Anaerobic conditions are thought to be the cause of the slow rate of stabilization of landfills. Settlement is considered to be a measure of the degree of completion of landfill stabilization. The greater the settlement that has taken place, the more stabilized the fill. The normal settlement of a sanitary landfill appears to be an exponential function of time with most of the total settlement completed within the first three years. Merz and Stone found that the greatest settlement takes place the first month after placement. After the third month the settlement rate is uniformly small. They also found that aerobic fills maintain active decomposition better than anaerobic fills and have settlement rates as much as four times as great as anaerobic fills.

The physical consolidation or settlement of the landfill is the result of both decomposition of organic materials and the collapse of voids created by cans and containers that rust or decay. It has been found that the amount of settlement of a refuse disposal area depends, in addition to the amount of water reaching the site, upon the initial conditions of the refuse placement. The greater the density in situ, the less the settlement. The following is a discussion of the anaerobic landfill environment as reported in a SED report: "The Seattle (Washington) Sanitary landfill test data indicate that considerable biological action may occur in a landfill, which can assist in achieving maximum refuse volume reduction. The use of large quantities of soil in a landfill, although desirable for sanitary control, unfortunately reduces the storage volume available for refuse disposal. Optimum uses of scarce land for sanitary fill type refuse disposal achieves high initial maximum compaction followed by ultimate conversion of most organic solids to gases and liquids accompanied by optimum settlement so that additional refuse could be supplied to the surface of the same site."

### (3) Aerobic Landfilling

Preliminary studies by Stone of "controlled aeration biologic incineration" or aerated landfill techniques have indicated significant cost savings when compared to conventional sanitary landfill (anaerobic) and composting. Essentially the aerobic cells are divided into two sections: the aeration cell area where the air is distributed into the refuse, and the residue cell area for disposal of the oxidized waste residue. In addition to the above biologic system, Stone also investigated a "high rate oxidation incineration" non-biologic landfill method of decomposition of solid wastes.

"Household solid waste required some three months to undergo significant cellulose oxidation and decomposition. Well-oxidized residue was substantially free of the most readily decomposable fraction. The oxidized residue was easily excavated, transferred, and compacted for final disposal in the residue cell, where subsequent anaerobic gas generation and settlement was minimal. Some 20% to 40% volume reduction was achieved in the aerobic test cell, depending upon the amount and type of organics in the raw solid waste. Greater decomposition occurred with residential organic solid waste materials than with the largely commercial or demolition origin inert type wastes. However, even rubber tires and plastics were observed to be oxidized, probably due to the high temperatures (to 160°F.) and other oxidizing effects of the aerobic process."

### (4) Landfill Leachates

Quasim and Burchinal have presented a generalized method for the theoretical determination of the concentrations of some of the easily extractable materials leached from sanitary landfills. Given the physical parameters of the land fill; i.e., depth, density, etc., the theoretical chloride concentrates can be determined and then from these concentrations, the concentrations of the various other species, using their known ratios to chloride concentration, can be predicted. The same authors in a follow-up article conclude from their examination of simulated landfill columns of various depths that deep fills, under similar conditions of precipitation and percolation, consume more water before leaching occurs, take a longer time to decompose, and the bulk of extracted material is distributed over a longer period. They conclude, "Therefore deeper fills pose less of a pollutional problem than do the shallower fills, which may leach the bulk of pollution in a shorter period, thereby exceeding the dilutional capacity of the moving ground waters and degrading the water quality below desirable levels."

The State Water Pollution Control Board of California, in an analysis of landfill leachate samples, concluded that in general the ion concentrations in the leachate reached a maximum of 10-20 times the concentrations found in the original water. They recognized a large degree of physical holdback of inorganic materials in landfill as shown by the relatively slow reduction of the inorganic components in the leachate.

The National Coal Association is committeed to successful reclamation of mined lands and supports federal legislation to set minimum standards. Industry spokesmen told Congress in hearings in late 1971. Emphasis was placed upon the return of land in reclamation to productive or beneficial use -- a use compatible with the climate of the area, and the soil, vegetation, topography, uses and other conditions of the surrounding areas.

## C. Experimental Design

This investigation was directed towards determining some of the effects that landfilling operations would have in strip mine environments. Because of the paucity of information available on the quality of effluents from sanitary landfills, initial investigations were made to determine some of the parameters that might have immediate effects on altering a strip mine area. Once determined these data became the background axiomatic to the investigation of acid mine drainage abatement and alteration. The design was in three parts:

to produce landfill leachate; to produce acid mine drainage; and, to finally mix the two. Both batch and percolation techniques were used.

Because of the interest in possible organic interferences in acid mine drainage production, several parameters that reflected the organic content of the waste effluent from sanitary landfills were chosen to give as broad a study as possible. Effluent colors were monitored and any changes were assumed to reflect, qualitatively, changes in the concentrations of the various organic materials leached from the refuse. BOD and COD ratios were established; then COD's were monitored as reflections of the oxygen demanding nature of the refuse effluents. Dissolved organics were measured as total volative solids and provided the final organic parameter.

### (a) Landfill Simulation and Leachate Production

The landfill simulation experiments were made using vertical Plexiglass two inch inside diameter columns packed at a pressure of 100 pounds per square inch with milled raw municipal refuse obtained from a demonstration project in Madison, Wisconsin. The depth of the cells was varied from several inches to several feet. Water for percolation was applied at the upper surface of the vertical beds and allowed to infiltrate by gravity through the columns. There was a constant positive head at all times (the surface was kept under water) and the effluent from the bottom, i.e., the leachate, was collected as it drained from the columns. No attempt was made to isolate the cells microbiologically from the surrounding environmental organisms. None of the cells were inocculated with any special organisms. The cells were maintained at constant room temperature under ambient light conditions. All effluent was collected; and analyses were run on the composited samples at set volume intervals. As one volume was removed for testing a new volume was allowed to collect.

The refuse was used as received except that any large objects were picked out before compaction. This removed such items as crushed cans and large plastic packaging materials that would not fit into the columns or would not permit even compaction.

Gas production was measured with a ten liter battery jar into which six pounds of uncompacted refuse were dumped. A water level of between one and two inches was maintained at the bottom of the jar to provide a saturated humid environment. The jar was sealed with a sheet of Plexiglass. An outlet was provided with a connection apparatus consisting of a submerged U tube leading into a graduated cylinder filled with water. Gas production was read directly in milliliters under average atmospheric pressure and room temperature. The cell was maintained under ambient light conditions. In addition to information about gas production, the cell provided an opportunity for visual observations of the change in the nature of the refuse over the test period.

Submerged cells were constructed in addition to the simulated landfills as a way of generating volumes of landfill leachate within short periods of time. The leachate from these cells was not expected to contain the breakdown products of the microbial activity, but the overall chemical characteristics were expected to be similar. In addition to providing the leachate to be used in Phase Two, these tests were expected to provide data on the total available soluble constituents in the refuse. These cells were beakers used on a batch basis with known weights of refuse and known volumes of water. When the water was to be removed and new water added for further extraction, the cell was dumped on a vacuum filter. The solids collected, including the filter paper, were returned to the cell and fresh water was applied. The filtrate was saved and/or analyzed. The filter paper did not alter any of the parameters under consideration. The cells were covered with watch glasses to minimize evaporation and were kept in the dark at 20°C.

(b) AMD Percolation Tests

Percolation cells containing coal mine refuse for the production of acid mine drainage were constructed of Plexiglass two inch inside diameter columns filled and tamped with weighed amounts of acid washed pyritic coal wastes. An influent solution (as used by other researchers and similar to the composition of mineral ground water) was fed by finger pump to the surface of the cell waste material and allowed to infiltrate by gravity through the cell. It was collected as it dripped from the bottom of the column. The solution was made in ten liter batches and stored in carboys to be used as necessary. The design of the reactor system was such that the influent solution could be aerated or not, its temperature altered or a chemical feed introduced. The cells were used as a once through system but simple alterations permitted its use on a recycle system. The parameters monitored in this reaction cell system with coal mine refuse alone were sulfates (by turbidity), pH and acidity.

The coal mine refuse was personally collected from waste ridges surrounding Pottsville, Pennsylvania. In the laboratory the refuse was rough picked by hand to remove non-pyritic material. The remaining waste was broken up to a particle size passing a 6 mesh screen and retained by a 4 mesh screen.

Ferrobacillus bacteria were obtained from stock cultures kept by Lundgren at Syracuse University and were maintained by serial transfer in Silverman's 9K inorganic salt media. The stock cultures were mixed with samples collected in the field near Pottsville, Pennsylvania to develop a multi-species innoculum.

After initial experimentation indicated the base response of the coal mine refuse to the environmental conditions of the reactor cell system, new experiments were run to determine variations from this base response under altered conditions. The altered conditions in these experiments consisted of feeding landfill leachate produced in the submerged cells in place of the synthetic ground water. In this case, sulfates were no longer monitored because of the magnitude of their presence in the leachate influent. Under these conditions, cells were run continuously at a 500 ml./day rate of infiltration. When the influent was interrupted the cell was capped to prevent dessication.

### (c) CMR and Municipal Refuse - Submerged Cells

Three cells of milled raw municipal refuse mixed with washed coal mine refuse were maintained in a submerged environment with periodic flushing and replenishment of the surrounding water. As with the cells testing the effects of sludge described below, those parameters to be observed as reflecting production of acid mine drainage from the coal mine refuse were also highly concentrated in the municipal refuse. The expected fluctuations in the sulfate, iron, alkalinity, acidity and other parameters were expected to be minor and masked by the overwhelming magnitude of the changes due to the refuse alone. Therefore, as with the sludge cells, only the gross observation of pH was monitored. The system was contained in Nalgon beakers at room temperature and at ambient light conditions. Water loss due to evaporation was replaced between flushings.

Quantities of washed coal mine refuse known to contain pyritic material were submerged under undewatered digested sewage sludge. The sludge was expected to buffer the regions of pyritic chemical oxidation as well as inhibit the action of the iron pyrite oxidizing bacteria. Because of the high concentration of dissolved species no short term analyses were run on these cells. The primary parameter in this study was the increase in hydrogen ion concentration. Different dilutions of sludge to distilled water were used and a cell was constructed as a control using only distilled water. The cells were aerated from time to time and kept at room temperature and ambient light conditions within Nalgon beakers. The volumes of sludge solution were kept constant by addition of fresh distilled water upon any evaporative loss.

## D. Experimental Data and Results

### (a) Phase One Studies

Data from four submerged cells are presented. The cells contained 24, 10, 12 and 50.5 grams of milled refuse and were submerged in batch volumes of 250 milliliters of distilled water. Each new batch volume of water was allowed to remain in contact with the refuse in the cell for at least twelve hours. It was felt that this was sufficient excess time so that the concentrations of leachate constituents would be time independent. These constituents were COD, Solids, alkalinity, pH,and color. Color and solids data became less and less precise as the refuse began to physically fall apart in the cell slurry. Initial COD values ranged from 7,720 mg./l. for the 10 gm. cell to 28,564 mg./l. for the 50.5 gm. cell. The experiment was terminated when the leachate COD concentration was less than 15% of its initial value for each cell. The total volume (1.5 liters) associated with this reduction in COD concentration was the same for each cell regardless of its initial concentration or the weight of refuse. Tables in the reference thesis indicate the range in the values of the other parameters monitored in this experiment.

The percolation cells or simulated landfills could not be made to operate at depths of over ten inches at 100 psi compaction. The rate of evaporation exceeded the rate of infiltration at depths greater than ten inches. Data from three percolation cells is presented in tables in the reference thesis. One table shows BOD data for developing the BOD curve characteristics of this particular waste; another table lists COD data taken from the percolation cells to compare with that taken from submerged cells. The infiltration rate at 100 psi compaction for a ten inch cell depth was 34.16 in.$^3$/12 hours. The physical characteristics of the municipal refuse changed upon being subjected to leaching. The specific gravity decreased the natural moisture content and the waste became brittle and crumbly. Gas production occurred in spurts and the breakdown of materials within the cells was very slow. After five months newsprint was still legible and all objects seemed to have retained their original shape. The odor of the gas was intensely concentrated and exceedingly foul, not unexpectedly.

Finally, a batch activated sludge system was operated using excess air and activated seed and a ten hour detention time yielding an 86% COD reduction. Much of the data developed in this phase of the overall problem was background information for the further experimentation in Phase Two Studies.

(b) Phase Two Studies

Paralleling the Phase One Studies, Phase Two experimentation included both submerged and percolation cells. Two sets of submerged cell data were collected, one using coal mine refuse and digested municipal sewage sludge, the other coal mine refuse and the milled municipal refuse used in Phase One. All cells were 500 ml. beakers. Each set of four cells included a control containing nothing but CMR and water and three other cells containing varying amounts of either sewage sludge or municipal milled refuse. None of the cells were sterilized. In the submerged experimentation, only pH was monitored. The control cells for both sets had initial pH readings of 7.8 and the pH of both fell abruptly to under pH 4, characteristic of phritic oxidation. In all cells containing municipal refuse or sludge the pH level remained above six.

Two pairs of percolation studies are presented here. Both parts were performed in duplicate. The parameters monitored were pH acidity/alkalinity and initial and final $SO_4$ ionic concentration. To the first pair aerated synthetic ground water was applied to two systems: one innoculated with Ferrobacillus and one sterile. The duplicate pairs gave comparable results. The pH values dropped from 6.5 to 4.0 in the sterile systems, with increasing sulfate concentrations and slightly increasing acidity concentration. In the innoculated systems, the pH drop was more pronounced, 6.3 to 3.5 with a much greater increase in sulfates and acidity.

To the second pair of percolation studies, a composite aerated landfill leachate was applied to the innoculated and sterile pairs of cells. Sulfate was not monitored here because it was felt the high concentration in the leachate influent would mask any changes due to puritic oxidation. In both systems, the initial pH was seven and did not drop below a level of pH 6.8.

## E. Discussion of Results

Questions regarding the ability to extrapolate results from miniature laboratory scale systems may apply to the experiments in this report. Are the samples of refuse, municipal and industrial, representative of the wastes that cause the specific pollution of the environment under discussion in this report? What effect does disturbing and then repacking the refuse samples have on their value for an experimental study? Care was taken to use representative samples. With respect to Phase One Studies, the hammermilling of municipal refuse is itself a homogenizing process. With respect to Phase Two, initial experiments trying to produce the acid mine drainage phenomenon in the laboratory at

Syracuse University were unsuccessful. Effluents were almost the same composition as influents. Values did not approach the values reported in the literature. Because Syracuse is not in geographic proximity to the acid mine drainage areas, field experiments could not be conducted on existing acid mine drainage. The coal mine refuse available to this study was sent from sources initially not particularly aware of the ultimate use of the material. Much of the refuse was of little value. After much effort, the researcher was able to define what was actually wanted. A personal visit was made to an area known for its acid drainage problems. Even there, the various mining engineers seemed to be unaware of the type of material needed. Samples selected haphazardly by the researchers and shipped to Syracuse at last yielded the necessary pyritic refuse material that the literature indicated was the source of the acid mine drainage problem. Experimentation with this material in which the pyrites could actually be seen again yielded disappointing results. It was discovered that the problem in this case lay in the highly alkaline facing material in the coal refuse samples. Simple washing in hydrochloric acid drove off this alkalinity and made available the pyritic residues. At this point, experimentation proceeded with an expectation of workable results.

### (a) Phase One Studies

It is of interest to examine the rates of leaching versus the initial weight of refuse being leached in this phase of experiments. Quasin and Burchinal experimenting on field scale lysimeters conclude that deeper fills show lesser reduction rates, and deeper fills leach lower concentrations per unit depth than do shallower fills. The submerged cell results indicate no such correlation with respect to unit leachates. COD values do not vary consistently with total weight in the cell. Percolation cells indicate an opposite correlation. The greater the depth the greater the reduction rates of leachate concentrations (i.e. same volume of solvent passed with different initial concentrations gives equal percentage reductions).

It is generally recognized that gas production in sanitary landfills is observed for over 6 to 24 months after placement. The data on gas production in this report is of interest therefore because it indicates the milling process on municipal refuse does not eliminate gas production. The ability of landfill leachate to be treated by a modified activated sludge process is indicated by the reduction of COD on one hand, and the reduction of the humic acid colors on the other.

(b) Phase Two Studies

In the percolation studies of pure coal mine refuse a biologic mat of bacteria and fungi developed clogging the tubes and sealing the upper surface of the refuse in the reactor. Autoclaving of the apparatus and of the refuse was not possible. The apparatus was made up largely of non-heat resistant plastic materials. It was feared that autoclaving of the coal mine refuse would stimulate chemical oxidation of the pyrites before percolation studies could be made. In the end the procedure was to permit the growth of the biologic mat but periodically break it up with a spatula. At no point were the unseeded reactor cells contaminated by the Ferrobacillus even though they may have been contaminated by other sources.

With respect to the limited number of parameters followed in any of the experiments involving the acid mine drainage phase of the paper, it was felt that these selected parameters were key indicators of acid mine drainage as well as being rather simple analytically. This latter fact was important because many tests were run on trial basis to see if these tests would yield significant data. It should be noted, in addition, that in the literature researchers in this field have usually minimized the selection of parameters presumably from similar data.

It was decided that although the ferrous-ferric ion oxidation rate had been determined by some authors to be the rate determining step, and therefore a controlling reaction in the abatement of acid mine drainage, that a more generalized approach than one specifically directed at preventing that oxidation would be of more practical value in the field. Once a few gross abatement techniques had been developed it was expected that close examination of them would yield information that such specific inhibition theoretically discussed in the literature had in fact occurred. On the other hand, a perfect theoretical inhibition of the pyritic oxidation might have absolutely no practical value in the field. Therefore, a strictly empirical approach was carried out with a subconscious awareness of the various theoretical requirements. Discarded in this context were several sets of data investigating the alternation of the oxidation potential of a solution of synthetic acid mine drainage because they could not be monitored in a multimolecular system containing coal mine refuse, bacteria and other materials.

The actual selection of laboratory approaches relied heavily on the concept of mutual beneficial effects arising from independently negative value materials. Sewage sludge and municipal refuse are two negative value materials presently available everywhere. Any beneficial use to which they can be put offsets the costs of their disposal, maximizing to a point where benefits gained from their disposal become greater than the costs of disposal. This is a positive goal and the directions in which these series of experiments were aimed. The result of work done with both sludge and municipal refuse are reported with an emphasis on the municipal refuse due to the general lack of knowledge about its leachate production and inhibitive effects.

The data gathered from the experiments indicate without doubt that there is an amelioration of the acid drainage problem, although the extent and practicality of the alterations are not fully defined. It is difficult from a bench study to conclude what may, in the field in Appalachia, be realistic. Is the scale of the ratio of municipal refuse to coal mine refuse a reasonable figure with respect to the volumes of coal mine refuse or the volumes of municipal refuse existing in the field? Would the pollution arising from the municipal refuse drainage, so clearly demonstrated in the first phase of these experiments become a greater threat to an already polluted environment? In other words, the optimization of the technique of acid mine drainage alteration has not been studied as it must be before any generalizations concerning its full application can be made.

The engineering estimates as to the causes of alteration of production can be mentioned. The high oxygen demand of any solutions in contacting municipal refuse will create an environment unsuited for the Ferrobacillus bacteria. The high organic concentration (TVS) is known in many cases to interfere with the activity of chemosynthetic autotrophs of which Ferrobacillus is a member. The buffering capacity of the leachate maintains a chemical environment (pH) unsuitable to the Ferrobacillus.

## F. Conclusions

(a) Small bench scale simulated landfills are useful as analogies to field simulated models and full scale operations with respect to all applicable parameters except gas production. The values of the various constituents leached by infiltrating water are well within the limited values quoted in the literature.

(b) Water infiltrating through compacted and uncompacted municipal refuse poses an immense threat of high oxygen demand and dissolved organic pollution to any receiving waterways.

(c) On the bench scale, maximum concentrations of contaminants arise immediately in contrast to the lag period reported in the literature. In addition, there was observed not to be a depth dependent reduction in contaminant strength per unit refuse leached as reported in the same literature. The rates of removal rapidly "level off" to values still large enough to pose threats to water resources. Reductions of these values to those of "clean" water did not occur within the experimental time periods.

(d) Small bench models to produce acid mine drainage from coal mine refuse will not supply information quantitatively accurate enough on which to base engineering decisions. Results of those bench models must be optimized in the field on a much greater scale. Practical approaches to acid mine drainage abatement and coal mine refuse disposal must still be determined on a gross scale.

(e) On the bench scale in the presence of milled municipal refuse and its leachates there is shown to be an abrupt alteration in the production of acid mine wastewaters and/or its production from pyritic coal mine refuse.

## G. Recommendations

(a) The bench scale simulated landfill and the submerged refuse cell techniques should be compared with larger scale models utilizing identical refuse materials in order to demonstrate to what point the bench scale model functions as a full scale operating model.

(b) On the basis of qualitatively successful laboratory experiments, scaling up to a field size study of acid mine drainage inhibition using municipal refuse and refuse leachates is recommended.

(c) Further laboratory investigations are warranted to determine whether the observed inhibitions in acid mine drainage production are primarily biologic or physiochemical in nature. Once the mechanism is isolated in the laboratory and verified in the field, a search can be made to determine other waste sources that can potentially supply the same inhibition.

## H. References and Appendices

The reference thesis on which this chapter is based contains 27 tables of data and two figures. The appendix lists 93 pertinent literature citations.

The complete thesis is available through the Solid Waste Information Retrieval System (SWIRS) or on an Inter-Library Loan from Syracuse University.

# CHAPTER 10. "THE USE OF SOLID INDUSTRIAL WASTES IN THE PREPARATION OF CONSTRUCTION MATERIALS," M.S. THESIS, JYH-CHAU LIN (JUNE 1971)

## A. Introduction

The United States, as a nation, presently generates more than 3-1/2 billion tons of solid waste annually; this is approximately 100 pounds per person per day. Approximately 90 pounds of this waste results from agricultural, animal, and mineral industries with the mineral industry being the most prolific source. The remaining 10 pounds are attributed to residential, commercial, municipal, and other industrial activities. Most solid wastes are treated through land disposal or incineration, and include dumping, burning, or burying in the disposal process. This large amount of solid waste not only requires a great deal of money to dispose of, but also wastes much valuable material.

In this country, the vacancy rate for all types of housing is rising dangerously. In 1961, about 60,000 apartment units were erected in New York City. But in 1968, only 15,000 were completed - a 75 per cent drop in just 7 years. The United States national goal, established by Congress in 1968, was 26 million houses and apartments in 10 years. With the booming post World War II baby crop graduating from school and breeding babies of their own, estimates are that over the next 30 years, nearly as many units as now exist in the entire country will have to be built. One of the easiest and most logical solutions to this urgent problem is to design lightweight and low cost precast concrete modules. To achieve this goal using solid waste as a structural material for their construction is feasible, efficient, practical and economical.

The main objective of this research was to evaluate the possibility of using industrial solid wastes, such as paper, Red Dog, Solvay Process Waste, and glass fiber in concrete construction. Paper and Red Dog were treated as coarse fillers in lightweight concrete. Solvay Waste was used as a fine aggregate to substitute for normal sand. Glass fiber was added to concrete as a reinforcement to increase concrete's tensile strength.

Paper and Red Dog were used in this research program to demonstrate the feasibility of producing lightweight building materials suitable both for structural and insulating applications. Solvay Waste is a waste product of the Solvay process industry and has been deposited in waste beds for over 50 years. The beds occupy a large area of ground and this waste has no constructive use. If it could be used in construction, not only would the waste beds be eliminated but also a large area of valuable land would become available for other uses.

The tensile strength of Portland cement concrete is approximately 10 per cent of its compressive strength. In structural concrete the tensile strength is increased by the addition of a steel reinforcing bar. But in many applications, such as in highway pavements, curbs, and sidewalks, reinforcing bars are not feasible or practical because tensile strength requirements are lower and cracking and spalling are of greater concern. Glass fiber is an inorganic material, good in tension but poor in bending and shearing. The addition of inorganic fiber was made in an effort to overcome the relatively low tensile strength of the concrete.

## B. Background Review

Waste in this study refers to useless, unwanted or discarded materials and includes any superfluous or rejected material either solid, liquid, or gas. Atmospheric wastes consist of particulate matter, such as dust, smoke, fumes, and gases. Liquid wastes consist mainly of sewage and industrial wastewaters, containing both dissolved and suspended matter. Solid wastes are classed as refuse.

At the present time, as a nation, more than 3-1/2 billion tons of solid waste are generated each year. Of this 3-1/2 billion tons, approximately 90 per cent result from agriculture, animal, and mineral industrial activities. The remaining 10 per cent come from residential, commercial, municipal, and other industrial activities. Of this 10% current estimates show that public and private agencies in the United States collect an average of 5.32 pounds per person per day of solid waste. In other words, more than 190 million tons per year of solid waste are collected by public and private agencies in the United States alone. By 1980, 235 million people are expected to generate 8 pounds per person per day of solid waste or more than 340 million tons per year.

Municipal refuse is a complex substance both physically and chemically. In 1970, the quantity of solid waste generated by United States municipalities alone was estimated at 0.95 ton per person per year. This figure did not include a large portion of commercial and industrial solid waste. If the contribution from these sources were included, the average municipal solid waste produced each year would total 4.5 tons per person. Recently, typical data showed that each year Americans discarded over 48 billion metal containers, 7 million passenger cars, trucks and buses, 30 million tons of paper, and 28 billion jars and bottles. Most of this refuse is discarded or disposed of by landfill and incineration. If these solid wastes can be used, not only can income accrue from their sale but there will also be a reduction in the cost of disposal.

### (a) Solid Waste Disposal Methods

#### (1) Landfill

There are three basic types of landfill systems in wide use today. The most primitive is the unrestricted dump which has proven to create more problems than it solves. A second method, which is an alternative to dumping, is shredding. The refuse is literally homogenized at the landfill site by large shredding machines. However, shredded waste may decompose rapidly and generate methane gas which can cause fires. The ordinary shredder cannot take large items like refrigerators or demolition materials. Shredding is a slow costly process requiring large amounts of power. Although shredding somewhat reduces the volume of solid waste, only further compacting will actually densify it. The third method is the "sanitary landfill" which is a controlled method of refuse disposal in which solid waste is dumped in a natural, man-made depression or trench, or at ground level and compacted to the smallest practical volume and covered with compacted earth or other material in a systematic and sanitary manner.

A landfill for municipal solid waste must be properly located to avoid contamination of air, surface water and ground water. Suitable land within economic range of the source of the refuse is required and the site must be of such a nature that pollution can be prevented by the application of available technology. Where these requirements cannot be met, incineration will most often be the best alternative for disposing of municipal refuse, and use of incineration seems likely to grow.

### (2) Incineration

Incineration is the process of reducing combustible wastes to a stable, odor-free, sanitary residue by high-temperature burning. There are many virtues to this popular refuse-burning technique. It can be made pollution-free, does not require much land, nor does it depend on weather conditions. It can also be located in urban industrial areas to save hauling. Generally, combustion is 85 - 90% complete for the combustible materials. The temperature in the combustion chamber bed should reach 2500° F, or more. Modern "total incineration" can convert refuse to solidified slag and flue gases and the volume reduction of solid waste may reach approximately 97.5%. The incinerator produces normal primary products of combustion - carbon dioxide and water, as well as oxides of sulfur and nitrogen and other gaseous air pollutants which may be generated. It also produces fly ash, unburned solid residue, and heat from combustion.

The installation and maintenance of devices aimed at preventing air pollution by proper control of combustion and stack effluents substantially increases the cost of incineration. The cost has been almost doubled for small units (from 240 to 450 tons of refuse per day) and increased up to 30 per cent for large units (over 500 tons per day). About 18% of municipal solid wastes are currently handled by incineration.

(3) Composting

Composting is a means for the biochemical degradation of organic materials to a sanitary, nuisance-free, humus-like product. Modern scientific composting has been described as a rapid but partial decomposition of moist, solid, organic matter by the use of aerobic micro-organisms under controlled conditions. Composting operations include three basic steps: (1) refuse preparation; (2) stabilization of organic material by aerobic micro-organisms; and, (3) product upgrading. Refuse is presorted to remove noncompostible materials or those that might have salvage value, such as paper, cardboard, rags, metal, and glass. The refuse is then ground to improve the efficiency of the aerobic digestion process. The ground material is stacked in long and narrow piles (windrows) on the ground or placed in a mechanical system where it is degraded biologically to a humus that contains about 1 per cent or less of the primary plant nutrients (nitrogen, phosphorous and potassium).

Various solid wastes can be composted if a major percentage of their composition is organic. Solid wastes such as refuse coming from the food and packing industries, fermentation processes, paper mills and wood processing plants, and various matural or synthetic fiber mills are suitable for treatment by the composting method. Of the waste that enters a composting plant, more than 75 per cent goes into the digestion process and one-third to one-half of the latter amount becomes compost.

Composting municipal refuse to produce low-grade fertilizer is generally unsuccessful in the U. S. A. - mainly because it has been difficult to sell the compost at a realistic price. Moreover, composting may be a costly process which can pollute the air with a noxious smell. As a result, the method has achieved greater success in countries where synthetic fertilizers are not readily available.

### (4) Ocean Disposal

Ocean disposal is a method of dumping solid waste into the ocean to provide for natural self-purification. The total amount of waste dumped into the ocean between 1949 and 1968 has increased from an average of 1.7 million tons at the beginning of that period to an average of 37 million tons at the end. However, the effects of this procedure on ocean ecology have become apparent. It is clear that the ocean is not an unlimited refuse disposal site. Unlimited ocean dumping is prohibited now except when permits for such waste disposal are obtained from the administrator of the Environmental Protection Agency.

### (5) Swine Feeding

Feeding of garbage to swine is a disposal method in which aesthetics and the potential for disease are public health considerations.

Some of the health problems result from the operation of a farm on which swine are fed on garbage while others come from the resulting pork products when they are put on the market.

Prior to 1950, this method of disposal was practical with domestic and industrial refuse. Recently, however, the cost of separate collection of garbage is a deterrent to disposal by this method in large urban communities. Nevertheless, it has been estimated that about 25 per cent of the garbage portion of solid municipal waste was being utilized as swine-feed in the United States in 1966.

(6) Reuse

Most reusable refuse is found in rubbish, although garbage and ashes also contain some. Of the items found in rubbish, some items have resale value and others have little or none. Salvageable materials include rags, newspapers, mixed paper, cardboard, books and magazines, bottles, rubber, ferrous metals, nonferrous metals and glass.

Paper and paper products make up the largest proportion of salvageable materials in the refuse produced in the United States and the amount is increasing. Each day about 2.3 pounds per person of combustible refuse is collected in an average United States city, 0.8 pound of which is paper. More than half of the rubbish collected and transported to dumps is paper and new methods to treat this solid waste are urgently needed. Recycling of newsprint is one of them. For every ton of reprocessed newsprint, the equivalent of 17 trees will be saved. This reused waste paper not only solves half of the solid waste problem but also conserves a large part of the natural forestland. However, only 20 per cent can be reused at the present time. The remaining 80 per cent is burned or buried and consequently permanently wasted.

Discarded tires can be a major source of rubber. Today, of the 100 million vehicular tires discarded annually in the United States, about 30 per cent are reclaimed and the remaining 70 per cent must be disposed of. However, reprocessing of rubber waste is declining because of the high cost of collection, transportation and reprocessing.

Disposal of the millions of automobiles that go out of service each year is another difficult problem. An abandoned automobile can provide an average of about 1.5 tons of salvageable metals. Ferrous materials are sold to steel mills as a salvaged material for reuse.

Metal containers are among the most important materials that can be salvaged, either before or after incineration. Non-returnable glass bottles and metal containers constitute a great percentage of domestic refuse. If the economics of collection, sorting and transportation of the materials can be resolved, these two wastes are easily reclaimable as sources of reusable materials.

At the present time, certain solid wastes are being used in construction; e.g., blast furnace slag and steel slag are being made into aggregates for road building and for concrete products of all kinds, fly ash from power stations is being used in aggregate, coal ash slag is being made into mineral wool comparable to other kinds os insulating material, sludges from paper and pulp manufacture and phosphate slime from fertilizers are used in gypsum wallboard, taconite iron ore tailings have been made into a foamed building material, coal mining wastes may be used for highway and shoulder materials, gold mine wastes may be made into building block materials, copper tailings used for ceramic tile or glass and waste glass or bottles crushed down to be used in road building.

Two main factors for consideration in the recycling of waste materials are first, and traditional, the matter of economics and secondly the violation of environmental conditions. Recycling is generally expensive particularly if the waste must be separated and processed. Consequently, this solution does not receive a great deal of attention unless the economics favor it. There seems to be no doubt that recycling of everything will become an absolute necessity in the near future, not only because of lack of space and facilities for disposal, but also because of the rate at which resources are being used up.

(b) Paper Reuse

Waste paper or paper stock is solid waste. In the high density population centers, paper and fiber content found present in collected solid waste can be run between 55 and 70 per cent. Since paper and fiber compose the major portion of municipal waste and since millions of tax dollars are required annually to collect and dispose of this waste, it is obvious that recycling or reusing paper and paper products will become an absolute necessity in the near future.

The paper and fiber field has given positive evidence that a great deal of good fiber can be secured from waste material and put back into the paper industry's operations. In 1970, the estimated 59 million tons of paper produced had only a recycling factor of about 20 per cent in the United States. This means that with the exception of a small percentage put into storage, some 40 million tons of paper and fiber has to be permanently disposed of each year.

In 1970, there were over 9 million tons of newsprint used in the United States. Collection and recycling, however, average out only to about 22 per cent. Even with this low percentage of paper recycled, several million acres of timber were saved.

The most serious deterrent to paper reuse is collection. Municipal garbage is full of paper and paper products but no satisfactory means of separating them from other rubbish and transporting them to collection sites is available. A partial resolution lies in paper drives. In general, these drives have taken four shapes. First, householders are asked to put their papers on the curb separately from other solid wastes. The paper is then collected by professional scavengers. Second, a voluntary program is inaugurated in which charities pick up the paper. A third, and maybe the most efficient method, is compulsory. Householders are told that they must separate papers from other refuse before collection time. Charities then pick up the papers and obtain some income for them while the city's refuse service cost is reduced. A fourth method is to put drop boxes in various locations to collect the paper. These drop boxes can be set out by churches, supermarkets, or placed by management in parking lots. After the boxes are full they may be sold to paper mills or other industries. This method has proven to be highly successful.

### (c) Solvay Waste Composition

Solvay Waste is a waste from the Solvay process industry which produces soda ash. This is a soft, clay-like extremely compressible, water pervious, and stratified material. Representative samples have been tested by the Solvay process industry. The samples were dried, passed through a 100 mesh screen, and analyzed by both wet chemical and x-ray methods.

The disposal of the solid waste produced by the Solvay Process presents a major problem to the industry as well as to the community hosting it. When this waste is disposed of on land, it requires a large area and many years to leach (over 50 years). To investigate the use of this solid waste in construction and to reduce the disposal problem are portions of this research work.

### (d) Lighweight Aggregate Concrete

#### (1) Lightweight Concrete Materials

Lightweight concrete has never been precisely defined. It is lighter than conventional concrete. Conventional concrete is the very familiar product made from sand and gravel which has for so long been a major building material. It has been suggested that lightweight concrete may be defined as a concrete which has been made from lightweight aggregate. This begs the question because lightweight aggregate has been defined as an aggregate which produces a lightweight concrete.

To resolve the difficulty presented by the definition of lightweight concrete, it may be considered as a concrete with a dry density of not more than 100 pounds per cubic foot. The conventional concrete usually weighs between 140 and 150 pounds per cubic foot. Short divides lightweight concrete into three groups: No-fines concrete -- concrete prepared by coarse aggregates such as gravel, crushed stone, coarse clinker, sintered pulverized-fuel ash, expanded clay or shale, expanded slate, foamed slag; Lightweight aggregate concrete -- concrete prepared by lightweight aggregates such as clinker, foamed slag, expanded clay, expanded shale, expanded slate, sintered pulverized-fuel ash, exfoliated vermiculite, expanded perlite, pumice, organic aggregates; and Aerated concrete -- air is introduced into the concrete composition to reduce its density, by two methods: Chemical aerating by aluminum powder, hydrogen peroxide or bleaching powder; and Foaming mixture - preformed foam, air-entrained foam.

The American Concrete Institute defines structural lightweight aggregate concrete as a concrete having a 28-day compressive strength in excess of 2500 pounds per square inch and a 28-day air-dry unit weight not exceeding

115 pounds per cubic foot. This definition is more restricted than the general definition. If the 28-day compressive strength does not exceed 2500 psi, the concrete can be used only in insulating applications rather than in structural uses.

In this research work, one set of experiments involves using waste paper or paper fiber coated with cement and spray lacquer or asphalt as an aggregate. This kind of aggregate is a non-mineral aggregate and will be called "artificial paper-ball aggregate". It differs from other materials given in various definitions of a lightweight aggregate.

Natural lightweight aggregates have been used since the time of the Romans. It is known that the 143 feet diameter dome of the Pantheon in Rome built in the second century A.D. was composed largely of cast in-situ concrete employing pumice aggregate.

Although a lightweight aggregate manufacturing process was patented as early as 1875, the real beginning of the use of expanded natural materials was in 1917 when Stephen J. Hayde developed a rotary kiln process for heat-expansion of shales and clays to form hard, lightweight materials. At about the same time, F. J. Straub pioneered in the use of bituminous coal cinders as an aggregate for the manufacture of concrete masonry units which attained a high volume of production following World War I.

Expanded clay aggregate was used in the United States for ship building in World War I particularly for reinforced lightweight concrete in the construction of ships and barges. Expanded clay and shale aggregates did not experience significant gains in utilization until after World War II when the natural sources of lightweight aggregate became inadequate, and could not supply the growing demand for lightweight concrete products.

With the advance of the sintering process, by which fine particles could be made to "weld" together into lumps, an important contribution to the rapid growth of the concrete industry was made. Now, lightweight concrete is a firmly established building material throughout the world. Most of these materials come from industrial solid wastes. If some other methods of treatment can be found to transform them into lightweight aggregates, the source of raw materials is nearly unlimited.

### (2) Desirable Properties

The advantages and properties of lightweight concrete include: Low bulk density, which can reduce dead load both in building and foundation and make handling and hauling much easier; High thermal insulation; High fire protection; Chemical inertness; High acoustic insulation; Good resistance to freezing and thawing; Low shrinkage on drying and minimum thermal changes; and, Uniform shape and size.

Lightweight concrete can substitute for conventional concrete in many circumstances. Moreover, it can be used in many applications where conventional concretes are not suitable. Lightweight concrete is suitable for the following applications: Curtain walls; Core materials for movable inner partitions; Reinforcing flooring; Fireproof insulating wall; Acoustic insulating wall; and, Foundations.

Concrete usually does not resist direct tensile forces because of its relatively low tensile strength and brittle nature. However, tensile stresses are important with regard to cracking. Most cracking, aside from that due to load or to settlement of parts of the structure, is caused by shrinkage from drying or temperature changes coupled with structural restraint. The tensile strength of concrete is approximately 10 per cent to 20 per cent depending upon age, type, and quality of the concrete. The higher the compressive strength the lower the relative tensile strength percentage. Generally, if it is desired to increase concrete's tensile strength, it is necessary to add steel reinforcing bars.

## C. Materials

The "concrete" test was made on a mixture of sand, cement, coarse fillers, and water. The main materials used in the experiment were sand, cement and additives. The sand was well graded natural sand of medium fineness. The cement was a commercial Type I Portland Cement. Additives used in the experiment included Red Dog, paper-ball, Solvay Waste, and glass fiber. Red Dog and paper-ball served as coarse fillers, Solvay Waste was used as a fine aggregate to substitute for sand, while glass fiber served as a reinforcement to increase concrete's tensile strength.

Red Dog is a kind of material from coal waste and is porous and lightweight. The density of pure Red Dog is 38 pounds per cubic foot, but in general, since the waste contains some impurities, such as sand, gravel and shale its density is almost double the pure waste - 71 pounds per cubic foot. In the experiment, Red Dog was crushed to about 1/2 inch size and mixed with sand and cement to make lightweight concrete. It was supplied by the Blue Coal Corporation of Ashley, Pennsylvania.

Paper-ball is another lightweight coarse filler used in the experiment. It was made from paper fiber. The density of torn, dried paper fiber is 11 pounds per cubic foot. The paper fibers were coated with cement and lacquer, or asphalt to make a round ball shape. The lacquer was an acrylic material. It was used to coat the round paper-balls with a plastic film which could protect the inner paper fibers from water and increased the paper-ball's hardness.

Cement coated the paper-balls with a thin shell, which also had waterproofing and hardening capabilities. Asphalt is an oily agent -- it can penetrate into paper fibers and bind them together and has similar characteristics. The density of the cement-lacquer coated paper-ball is 23 pounds per cubic foot while the asphalt coated is 21. Paper fibers were obtained from municipal newsprint and a paper factory.

Solvay Waste is a waste product of the Solvay Process Industry. The coarse portion of the waste is grey in color and more granular than the fine. The fine material is egg shell in color, clay-like when semi-moist, and almost gel-like when wet. The dry density of this material is 39 pounds per cubic foot. It contains a large portion of voids and is extremely compressible especially when it is dry. In the experiment, it was crushed down to a powder and served as a fine aggregate. Solvay Waste was taken from the Solvay Waste Beds of the Industrial Chemicals Division of Allied Chemical Corporation of Syracuse, New York.

Glass fiber is a long strand, inorganic matter. It is good in tension but poor in shear and has a brittle characteristic. In the experiment, it was cut to short pieces and added to concrete to increase concrete's tensile strength. The waste glass fiber was supplied by the Johns-Manville Company of Waterville, Ohio. Physical tests of the fibers were not performed.

### D. Experimental Procedures

The experiments were divided into two parts, compression tests and tension tests. The compression test specimens were made in 6 x 3 inch cylinder molds and were tested in a hydraulic compression testing machine. The tension test specimens were made in A.S.T.M. C190 one inch briquet molds and were tested with a briquet testing machine.

The purposes of this experimental work were twofold. First, experiments were conducted on paper, Red Dog, and Solvay Waste to determine the feasibility of using them to produce lightweight building materials suitable both for structural and insulating applications. Second, glass fiber waste was added to concrete as a reinforcement to increase concrete's tensile strength. It can be suitably used in highway pavements, curbs, sidewalks, and other applications.

(a) Artificial "Paper-Ball"

Paper fibers and newspapers were used as filler materials to substitute for mineral aggregate in concrete. Paper fibers were coated with cement and spray lacquer so that they would act as binding and waterproofing agents. The other binding agent used was asphalt. The procedures for making "paper-ball" were as follows: Torn up paper or paper fiber pieces were immersed in water to make the fibers soft and easy to combine; Various shapes of paper-balls were made by hand or machine and dried in an oven; The paper-balls were then coated with cement and spray lacquer or asphalt after the paper fibers completely dried; and, The treated paper-balls now became hard and waterproof, and could be used as a coarse filler mixed with cement and sand to make lightweight concrete.

(b) Red Dog

Red Dog is a porous and lightweight mineral material. In the experiment, it was crushed to about 1/2 inch in diameter to serve as a coarse aggregate and then mixed with cement and sand to make lightweight concrete.

(c) Solvay Waste

Solvay Waste is a clay-like material, very sticky when it absorbs water. In the experiment, it was used as a fine aggregate to substitute for sand. Before making concrete, Solvay Waste was dried in an oven, crushed to powder, then mixed with cement paste.

(d) Glass Fiber

Glass fiber is a long stranded, inorganic material with high tensile strength. The addition of this inorganic fiber to concrete was made in an effort to overcome the relatively low tensile strength of plain concrete. In the experiment, two procedures were used. In one, the glass fibers were cut to a one inch length and mixed as a filler with cement-sand mortar to make concrete. In the second, glass fibers were cut into three-inch long pieces and were bound together in bundles like steel bar reinforcement in concrete. Different results were achieved depending on glass fiber percentages and the method of mixing. All tension tests of the specimens were conducted using a briquet testing machine.

### (e) Compression and Tension Test Procedures

All the procedures for compression were run according to A.S.T.M. C109-47. The specimens were made in 3 x 6 inch cylinder molds and tested using a compression testing machine. Cement, sand, Solvay Waste, and Red Dog were used as fine and coarse aggregates in the experiment. Al the procedures for tension were run according to A.S.T.M. C190-44.

## E. Results

### (a) Paper-Ball

The artificial "paper-ball" lightweight aggregate studies were divided into two parts: one, paper fibers coated with asphalt. Cement was used as a binding agent, spray lacquer as a waterproofing agent, and asphalt was used to combine both of these characteristics. During the coating process, cement and spray lacquer deposited a thin shell around the paper-ball surface but asphalt petetrated into the paper fibers and bound them together. Asphalt was cheaper and easier to work with than spray lacquer. The asphalt used was an oily material unlike spray lacquer which could coat paper-balls with a plastic film. So the hardness of the asphalt coated paper-ball was less than that of cement-lacquer coated paper-ball and the resulting concrete exhibited the same characteristics. All cement, sand, and paper-ball mixing proportions were by volume, and all data obtained in this experiment were from an average of three specimens.

(1) Paper-ball coated with cement and spray lacquer

- (1-a) Mixing ratio:

  cement : sand : paper-ball = 1 : 1.5 : 4

  Paper-ball waterproof percentage 96%

  w/c (by weight) 0.7

  Dry density of concrete 95 lbs./cu.ft.

  Compressive strength (29 day curing) 523 lbs./sq.in.

- (1-b) Mixing ratio:

  cement : sand : paper-ball = 1 : 1.5 : 5

  Paper-ball waterproof percentage 98%

  w/c (by weight) 0.7

  Dry density of concrete 75 lbs./cu.ft.

  Compressive strength (28 day curing) 380 lbs./sq.in.

- (1-c) Mixing ratio:

  cement : sand : paper-ball = 1 : 2 : 4

  Paper-ball waterproof percentage 99%

  w/c (by weight) 0.7

  Dry density of concrete 83 lbs./cu.ft.

  Compressive strength (7 day curing) 255 lbs./sq.in.
  (14 day curing) 435 lbs./sq.in.
  (21 day curing) 540 lbs./sq.in.
  (28 day curing) 590 lbs./sq.in.

(2) Paper-ball coated with asphalt

- (2-a) Paper-ball (round)

  - (1) Mixing ratio:

    cement : sand : paper-ball = 1 : 2 : 4

Paper-ball waterproof percentage 95%

w/c (by weight) 0.7

Dry density of concrete 81 lbs./cu.ft.

Compressive strength (28 day curing) 176 lbs./sq.in.

(2-b) Mixing ratio:

cement : sand : paper-ball = 1 : 2 : 5

Paper-ball waterproof percentage 95%

w/c (by weight) 0.7

Dry density of concrete 75 lbs./cu.ft.

Compressive strength (28 day curing) 150 lbs./sq.in.

(2-c) Paper fibers made to various shapes

Mixing ratios:

cement : Paper fiber = 1 : 1, 1 : 2, 1 : 3
1 : 4, 1 : 5, 1 : 6

w/c (by weight) 0.7

Dry density of concrete and compressive strength (28 day curing) are as in the following table:

| Mixing Ratio Cement : Paper | Dry Density of Concrete lbs./cu.ft. | Compressive Strength lbs./sq.in. |
|---|---|---|
| 1 : 1 | 93 | 252 |
| 1 : 2 | 73 | 95 |
| 1 : 3 | 61 | 45 |
| 1 : 4 | 59 | 38 |
| 1 : 5 | 57 | 37 |
| 1 : 6 | 46 | 21 |

(b) Solvay Waste

In this experiment, Solvay Waste was used to substitute for sand in making concrete. Solvay Waste was mixed with cement; the mixing ratios of cement to Solvay Waste were set at 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 6 by volume. Tables and figures in the original thesis show the compressive strength of Solvay Waste concretes and cement-sand plain concretes respectively. These concretes were made under the same conditions and were tested at a 28 day curing time.

(c) Red Dog

Red Dog like other mineral lightweight aggregates was porous, hard, and lightweight. Most of this industrial solid waste from the coal industry contained some impurities, such as gravel, sand, shale, etc. Due to these impurities, the density of impure Red Dog was almost twice that of pure Red Dog. Experimental data of Red Dog mixed with cement, sand, and paper-ball were as follows:

(1) Pure Red Dog mixed with Cement
Mixing ratio: cement : Red Dog = 1 : 4
w/c (by weight) 0.7
Dry density of concrete 80 lbs./cu.ft.
Compressive strength (21 day curing) 863 lbs./sq.in.
(28 day curing) 920 lbs./sq.in.

(2) Impure Red Dog mixed with cement and sand
(2-a) Mixing ratio:

cement : sand : Red Dog = 1 : 1.5 : 5

w/c (by weight) 0.7

Dry density of concrete 108 lbs./cu.ft.

Compressive strength (7 day curing) 1250 lb./sq.in.
(14 day curing) 1290 lbs./sq.in.
(21 day curing) 1330 lbs./sq.in.
(28 day curing) 1590 lbs./sq.in.

(2-b) Mixing ratio:

cement : sand : Red Dog = 1 : 2 : 5

w/c (by weight) 0.7

Dry density of concrete 117 lbs./cu.ft.

Compressive strength (7 day curing) 1500 lbs./sq.in.
(14 day curing) 1535 lbs./sq.in.
(21 day curing) 1560 lbs./sq.in.
(28 day curing) 1620 lbs./sq.in.

(3) Impure Red Dog mixed with paper-ball and cement

Mixing ratio:

cement : Red Dog : paper-ball = 1 : 2 : 4

w/c (by weight) 0.7

Dry density of concrete 65 lbs./cu.ft.

Compressive strength (7 day curing) 117 lbs./sq.in.
(14 day curing) 176 lbs./sq.in.
(21 day curing) 210 lbs./sq.in.
(28 day curing) 230 lbs./sq.in.

(d) Glass Fiber

In order to compare the tensile strength of glass fiber reinforced concrete with plain concrete, all cement-sand ratios and water contents of briquet specimens were set at 1 : 3 and 0.7 by weight respectively. Coarse aggregates were not used in order to avoid the uncertainties of non-homogeniety. Six standard A.S.T.M. C190 one inch briquet specimens were prepared for each test. The batch weight was:

| | |
|---|---|
| cement | 600 gr. |
| sand | 1800 gr. |
| water | 420 cc. |
| glass fiber | 12 gr., 24 gr., 36 gr. |

The percentages of glass fiber used in the specimens were 1, 2, and 3% by volume. All of the specimens were cured in water for 7 and 28 days prior to testing. The ultimate tensile strengths of the briquet specimens tested are given in the tables and figures in the original thesis.

## F. Discussion of Results

Paper-balls used as aggregate were coated with a plastic film of cement and spray lacquer. This thin shell held the paper fibers together and protected them sufficiently to keep inner fibers dry. However, the bond between this film and the concrete was not very good. When "paper-ball" lightweight concrete was compressed to failure, the concrete collapsed along the boundary surface of this thin film and concrete but the paper-ball aggregate itself was seldom broken. It was concluded that the paper-ball aggregate was relatively stronger than the binding force between spray plastic film and concrete. The waterproof characteristics of paper-balls were important. When the paper-fibers absorbed water, the paper-balls became soft, and the resulting concrete's compressive strength decreased. Since the paper fibers were dry and could easily absorb water, it was difficult to make them perfectly waterproof. Alphalt was also used as a waterproofing agent in this experiment. It penetrated into the paper fibers and bound them together. However, the hardness of the paper-balls and the waterproofing property of asphalt was less effective than cement-lacquer agents. The efficiency of using cement and spray lacquer was much better than asphalt.

Solvay Waste was a clay-like material. Before making concrete, it was dried in an oven and then crushed to a powder. With this treatment, it became porous, compressible, and cement-like. During the mixing process it absorbed more water than cement did and became a sticky paste. The experimental data show that the ratio of compressive strength of Solvay Waste concrete to plain concrete for the 1 : 1 to 1 : 6 mixes remained approximately constant. The binding force between Solvay Waste and cement paste was weak. The Solvay Waste concrete speciment were not hard and were easy to crack although they were lighter than conventional concrete.

Red Dog contained some impurities, such as sand, gravel, and shale. The density and hardness of these impurities were greater than pure Red Dog. Therefore, the density of impure Red Dog concrete was greater and the concrete's compressive strength was also stronger than the strength of pure Red Dog. The binding force between Red Dog and cement-sand mortar was good. The compressive strength of 7 day Red Dog concrete in a 1 : 1.5 : 5 volume mixing ratio had 80 per cent of the 28 day's strength. With a 1 : 2 : 5 mix, the figure was as high as 93 per cent. For some emergency and temporary construction applications, this kind of lightweight concrete may be applicable.

The objective of mixing Red Dog, paper-ball, and cement to make concrete was to make use of paper-ball's light weight and the good binding capacity of Red Dog with cement. Since there was a lack of fine filler, the density of concrete was low enough; however, the compressive strength was inadequate.

Bond strength between glass fiber and concrete was very important. The bond arose primarily from friction and adhesion between the two materials. It also may be affected by the shrinkage of the concrete relative to the glass fiber. If the friction and adhesion between fiber and concrete were perfect, the two materials would break simultaneously when the concrete supported a tensile force to failure. All glass fibers added in the experiment, except those which were arranged in the concrete by mixing, failed only through slippage.

The bond involves not only the properties of the concrete and the mechanical characteristics of the glass fiber but also the position of the glass fiber and its arrangement in the concrete member. The arrangement of all bundles in the concrete was parallel to the direction of tensile force. The experimental data show that the glass fibers mixed with the concrete produced a lower tensile strength than the bundles did. This may be accounted for by the differences in the position and arrangement of the glass fibers. The experimental data show that the more glass fiber added to the concrete the greater tensile strength obtained. However, there was a limit to the amount of fiber which would be added and still obtain a workable concrete mixture.

## G. Conclusions

(a) The objective of investigating the use of waste paper in construction is to offer a partial solution to the problem of its disposal and to make use of the light weight of the paper fibers. The addition of artificial "paper-ball" in concrete as a lightweight aggregate is feasible and practical. Because the compressive strength of this lightweight aggregate concrete is not sufficient, the aggregate can only be used in insulating applications rather than for structural uses at the present time.

(b) Red Dog is a good concrete filler. The bonding force between it and cement-sand mortar is positive. It can be used in foundations, structural members, and road building applications to serve as a lightweight aggregate.

(c) Solvay Waste is a soft, sensitive material resembling a clay. The binding force between it and cement paste is not good enough to support large loads. When absorbing water, it becomes gel-like and is too sticky for practical use. It is doubtful that it can be used as a filler to substitute for sand.

(d) Glass fiber is a high tensile strength inorganic material. The addition of glass fiber to concrete increases the concrete's tensile strength. It is especially feasible and efficient for use in highway pavements, curbs and sidewalk applications in which steel reinforcement is not available or too expensive for use.

(e) The tensile strength of glass fiber reinforced concrete in which glass fibers are arranged in bundles is greater than that of glass fibers added in a random mix.

(f) The addition of 2 per cent glass fiber to concrete can increase ordinary concrete's tensile strength over 50 per cent. The addition of glass fiber in concrete is feasible and efficient.

## H. Recommendations

The following recommendations are made for further experimentation and study:

(a) Study different agents to improve bonding and waterproofing paper fibers for use in paper-ball aggregates.

(b) Study chemical and physical characteristics of Red Dog for practical use both in-situ and pre-cast modules.

(c) Study to determine how inorganic glass fiber can best be used in concrete and to identify those applications for which it is particularly suitable.

(d) Further study of solid waste concrete, including drying shrinkage tests, shear resistance tests, impact tests, modulus of rupture and elasticity tests, splitting strength tests, and thermal expansion tests.

## I. References and Appendices

The reference thesis on which this chapter is based contains 6 figures of plotted experimental results. The data are contained in many unnumbered tables contiguous to the "Results" and "Discussion of Results" in addition to Appendices I, II, and III. A list of 22 pertinent references cited is appended.

The complete reference thesis is available through the Solid Waste Information Retrieval System (SWIRS) or on an Inter-Library Loan from Syracuse University.

# CHAPTER 11. "EFFECT OF HUMUS MATTER ON RETENTION OF NITROGEN FERTILIZERS IN SOILS" M.S. THESIS, MOHINDER KUMAR SAINI (AUGUST 1971)

## A. Introduction

Excessive problems have been reported in the literature in the past years regarding water quality resulting from nutrients flowing into the streams, lakes, impounded water reservoirs, and underground waters. Within recent years, much concern has been expressed regarding the possible contamination of the United States' water bodies as a result of the use of agriculture fertilizers. The use of fertilizers increases the mineral nutrients in the soils where crops or any other vegetations are grown. The increase of mineral nutrients in soils is due to addition of nitrogen, phosphorus, and potassium constituents along with trace elements. These nutrients stimulate the plant growth. The minerals present in fertilizers are utilized by the plants only when they are soluble in the soil solution. When excessive moisture accumulates in the soil, these nutrients escape with flowing water in the form of percolation (leaching) into the ground water or along with the surface run-off water. These escaping nutrients increase the nutrient level of the water bodies into which the agricultural run-off percolated water flows.

The nutrients from agricultural activities which contribute to the fertilization of water bodies are nitrogen and phosphorus. The presence of nitrogen and phosphorus compounds enhances the growth of aquatic plants in the water body; this process is called eutrophication. Eutrophication is the enrichment of the water bodies either natural or man-made sources. When enrichment of water bodies is due to man's activities like agriculture, it is called cultural eutrophication.

The compounds of nitrogen and phosphorus when present in water become the primary available sources of nutrients, thereby increasing the aquatic plant growth. Many other nutrients (such as calcium, potassium, magnesium, and sulfur - called secondary nutrients or macro-nutrients, and micro-nutrients such as boron, manganese, zinc, copper, iron, cobalt, chlorine, silicon, molybdenum, etc.) are also essential for the growth of some or all algae, and other aquatic plants. Nigrogen and phosphorus are the most important; without these the aquatic plant growth is not possible. Biggar and Corey mention that nitrogen and phosphorus are the only elements that have been definitely established as consistent growth limiting factors in natural waters.

Another school of thought is that carbon is the key element that controls algal growth in water environment. This idea has been supported by recent studies done by Lange of the University of Cincinnati and Kerr of the Water Quality Office of the Environmental Protection Agency.

It has not been very definitely established whether carbon or phosphorus is the key element. Both the carbon and phosphorus schools agree that algae need for growth sources of inorganic carbon, phosphorus, nitrogen and numerous other elements. Analyses of various algae have been made by Birge and Juday, and presented by Sawyer. These data shows that nitrogen and phosphorus are definitely major nutrients required by all algae.

Among the agricultural sources of water pollution, nitrogen has received particular attention because of the increased fertilizer use. Use of synthetic nitrogen fertilizers in the United States increased from 1 million tons in 1949 to 4.4 million tons in 1964 and to 6.8 million tons in 1968. In 1970, more than 8 million tons of nitrogen fertilizers are believed to have been used in the United States of America. Besides nitrogen from agricultural drainage, there are other sources of nitrogen which also contribute to the nitrogen build-up of water bodies. Various sources of nitrogen in water bodies will be discussed later.

The excess fertilization of receiving water bodies due to agricultural fertilizers flow can be an advantage in that more algae and aquatic plants can be produced which might aid in supporting a larger crop of fish in that water. However, there are more disadvantages associated with eutrophic waters. Some of the problems associated with eutrophic waters are: (1) Esthetic devaluation of the lake or the stream; (2) Inability to use the water body for recreational purposes; (3) Increased tastes, odors, color, and turbidity of eutrophic waters which make such a water body less desirable for water supply; (4) Blockage of intake screens due to floating scum, increased chlorine demand, and clogging of filters which raise the treatment cost to make the water potable; and, (5) Excess production of toxins in water due to blue green algae which render the water toxic and may result in human illness or in livestock death.

In this study, the use of humus matter to retain the flow of nitrogen fertilizers from agricultural land was investigated. Humus matter used in this study was digested sewage sludge. Digested sewage sludge (containing 70% moisture) from a community represents about 15% by weight of the total solids waste disposal problem. Use of digested sewage sludge along with synthetic fertilizers could retard the flow of nitrogen from agricultural land, thereby reducing the eutrophication process of a receiving water body from this activity of man. The combined use of chemical fertilizer and the digested sewage sludge can help to solve two problems - first, the disposal of sewage sludge in a safe manner; and, second, water pollution abatement from agricultural practices.

## B. Sources of Nitrogen in Soils and Waters

The presence of nitrogen in soils and in the water environment are due to both natural and man-made sources. Natural sources which contribute significant quantities of nitrogen compounds in the water are run-off and rainfall. Man-made sources of nitrogen in water bodies come from domestic and industrial wastes, run-off from agricultural land, farm animal wastes, and urban run-off. Natural sources of nitrogen in soils are rainfall and microbial fixation of nitrogen from the atmosphere; the man-made sources arise from addition of nitrogen fertilizers.

Compounds of nitrogen occur in many forms in the soils and water bodies. Among the numerous compounds of nitrogen, the particular species of primary concern in water in relation to the aquatic plant growth are: (1) Inorganic ammonium ions ($NH_4^+$); (2) Nitrite ions ($NO_2^-$); and, (3) Nitrate ions ($NO_3^-$).

In addition to these compounds, biologically significant nitrogen containing organic compounds such as proteins, amines and nucleic acids may be present in large concentrations either in solution or in suspended form. These organic compounds can be utilized by the plants only when they are broken down by microorganisms.

### (1) Forms and Amounts of Nitrogen

The compounds of nitrogen are widely distributed throughout the earth's environment. The atmosphere contains about 69 million pounds of atmospheric nitrogen over each acre of land surface. The total nitrogen content of most soils in the United States averages about 3,000 pounds per acre in the top 6-inch layer of the soils. Nitrogen fixing microorganisms utilize the atmospheric nitrogen and transfer this to the soils so it can be utilized by the plants for their growth. These microorganisms add about 100 pounds of nitrogen per acre from atmosphere to soil each year. The atmospheric nitrogen is largely in the form of elemental nitrogen ($N_2$), and the terrestrial nitrogen is largely in the form of stable organic nitrogen or complexed compounds. Both of these forms are only of limited availability for rapid plant growth. However, blue green algae are capable of utilizing the atmospheric nitrogen directly.

Most of the soluble nutrients that get into lakes and streams are first dissolved in water and then moved in solution to the waterways. Some nutrients are carried to streams and lakes as suspended particulate matter, and later converted to soluble forms. The following are the major sources of water soluble nitrogen:

(a) Fertilizers - The trend in the consumption of fertilizers in the United States shows an amazing growth in the use of synthetic nitrogen fertilizers since 1953. The use of nitrogen fertilizers has increased almost 600% since 1953. This increased use of fertilizers appears to be continuing. These increased amounts of nitrogen fertilizers increase the crop production. There is also an added opportunity for their loss to streams and lakes through leaching and run-off. The amount of nitrogen compounds produced in the United States in 1957 was over 5.5 billion pounds. Seventy-six per cent of the nitrogen compounds produced were used as fertilizers. Agricultural consumption of nitrogen compounds in 1969 was about 65% of the total nitrogen synthetically fixed

(b) Domestic Wastes Domestic wastes contain significant concentrations of nitrogen compounds. The primary sources of nitrogen in domestic wastewater are feces, urine, and waste food. Total nitrogen content discharged per person per year varies from 8 to 12 pounds with an average of about 11 pounds. In general, about 20 to 50 per cent of the total nitrogen in domestic waste is removed by the conventional treatment of the wastewater. The higher figures apply when fresh wastes are treated by complete treatment without returning the supernatant from sludge digesters to the effluent stream. Most of the effluents from domestic wastes flow into the streams or lakes. This flow increases the amount of nutrients in the streams and lakes.

(c) Farm Animal Wastes Farm animal wastes also contribute heavily to the nutrients of the water bodies. One cow generates as much waste as 17 human beings. Farm animals in the United States produce ten times as much wastes as humans. The amount of this nitrogen reaching water bodies is not known. It is assumed that flow of rain water from farm lands contributes heavily to the flow of nitrogen into the streams and lakes.

(d) Industrial Wastes Some industrial wastewaters contain significant quantities of nitrogen. Food processing industries dispose many nitrogen containing compounds into the water environment. Wastes from meat-packing industries contain high concentrations of proteins. The waste nitrogen from processing of one beef is about 1.5 pound, and from a hog is about 0.75 pound. Based on 1964 figures of 31 million cattle and 86 million hogs slaughtered, approximately 100 million pounds of nitrogen per year are contained in the wastes. A significant portion of this nitrogen probably reaches lakes and streams even after some biological treatment.

(e) Rainfall Some of the atmospheric nitrogen is fixed by lightning during rain storms and is brought to the earth through rainfall. Combustion of solid fuels like coal, or petroleum fuels in internal combustion engines add significant quantities of nitrogen compounds to the atmosphere; this nitrogen is brought down with precipitation. Veits quoted figures from the National Academy of Sciences for 1966 for addition of nitrogen oxides to the air; he stated that 2.5 million tons of nitrogen as the oxides are added to the air annually by the process of combustion, largely from internal combustion motors and power plants. Concentration of nitrogen compounds in the rain water has been determined by a number of investigators at various locations in the world. Biggar and Correy estimate that nitrogen derived from rainfall ranges between 1 and 19 pounds per acre per year at various locations, averaging 7 or 8 pounds. This nitrogen in run-off and percolated water becomes a steady and significant supply of nitrogen in the water bodies.

(f) Effects of Suspended Material The energy associated with the impact of falling rain drops tends to break down the soil particles at exposed soil surfaces. Water runs off the surface, then picks up these finer particles and carries them along with it, causing erosion. Nitrogen present in the soil in the form of organic matter is easily eroded and carried along with run-off. This form of nitrogen reaching streams and lakes may be attacked by microorganisms. In this decomposition process insoluble nitrogen is converted to soluble forms. No data are available to indicate the magnitude of this nitrogen going to water bodies.

(g) Other Sources Besides the above mentioned sources, there are a number of other sources such as discharges from municipal water treatment plants due to use of ammonia, or organic poly-electrolytes, water fowl, dust fall, etc., which also contribute nitrogen compounds to the water environment.

Estimates of total contribution of nitrogen to the water environment of the United States were made by the American Water Works Association. It appears that the agricultural run-off is the greatest single contributor of nitrogen to water bodies. The estimates show that agricultural contribution is from 2 to 17 billion pounds of nitrogen per year. Agricultural drainage is usually blamed for excessive flows of nitrogen to steams and lakes. However, there are many investigators who feel that the contribution of agricultural fertilizers in the nitrogen build-up of water bodies has been overstated. Garman states that the contribution of nitrate fertilizers to eutrophication and water pollution are relatively small compared to natural cycles of nitrogen in the ecosystem. He points out that the present annual usage of 7 million tons of nitrogen as fertilizers is considerably less than the 20 million tons of organic nitrogen calculated to have been lost annually from agricultural soils over the last 70 years. Smith writes that livestock concentrations have been found to me a more important source of nitrates in water supplies than chemical fertilizers.

Veits says that the commercial fertilizers are being blamed for substantial eutrophication when the available evidence is only circumstantial rather than direct. He also writes that the usual approach to the study of eutrophication of water has been to assign certain inputs to identifiable industries, municipal sewage plants, wash-off from storm sewers and rainfall, and to charge the rest by difference to agricultural run-off. In this agricultural run-off are included animal waste flushed from feed lots, fields and pastures, eroding soil, wash out of nutrients from dead vegetation, and fertilizers either in solution or adsorbed on eroding sediments. Fertilizers are only one part of the agricultural picture.

## C. Disposition of Nitrogen in Soils

Nitrogen fertilizers are the most important minerals applied to the soils to increase the crop yields in the agricultural farm management. The disposition of added nitrogen applied to the soils depends on a number of factors. Many things can happen to this nitrogen in the soil. Besides being used by the crop, nitrogen fertilizers may meet a number of other fates. When fertilizer nitrogen is applied to the soil, the fertilizer is dissolved in the soil solution and converted to ammonium or nitrate nitrogen, before it is utilized by the plants. There is some addition of nitrogen to the soils because of mineralization of organic matter. Many soil microorganisms are capable of degrading the organic matter present in the soil. Microbial decomposition of the organic matter results in the release of nitrogen in the ammonium form ($NH_4^+$), a process called ammonification. Under conditions of good aeration and favorable temperature, the ammonia released in this ammonification is oxidized by two species of bacteria to the nitrite form and then to the nitrate form. Bacteria which convert ammonia to nitrite are called Nitrosomonas and the ones which convert nitrite to nitrate are called Nitrobacter.

Nitrogen is also fixed by lightning in the atmosphere and brought into the soluble nitrogen pool by precipitation. Certain other organisms like Azotobacter and certain blue-green algae are capable of fixing atmospheric nitrogen. Presence of these microorganisms adds to the nitrogen pool of the soil, because after death and decay this nitrogen can be utilized by the plants. Nitrogen added to the soil either through the fertilizers or by the natural process of mineralization, precipitation or microbial fixation is either used by the plants or is lost by other mechanisms.

Soluble nitrogen in the soil is lost by leaching. This is commonly the main channel of loss of nitrogen. The loss is in the form of nitrates. The movement of this nitrate nitrogen is determined by the water movement. When rainfall is sufficient to cause water to percolate through the soil profile or cause a surface run-off, any nitrate present is gradually diluted and leached out of the top soil. Light rains do not remove the nitrates from the soil because the water does not move a long distance into the soil. Due to capillary action, salts again come towards the top surface. This upward movement is confined to the top 12 inches to 18 inches of the soil. Heavy rains either wash these nitrates from the top soil or move most of the nitrates present in the top soil to lower levels where they either accumulate, are lost to the ground water or are subjected to denitrification.

Burn and Dean have determined the factors which affect the movement of nitrates in the soils. These factors are: soil porosity, amount and movement of water, cations associated with the nitrates, physical placement, amount of nitrates added to soil, plant uptake, microbial activity and others.

Some of the soluble nitrogen is fixed either temporarily or permanently. Part of the nitrogen added is used by the soil microorganisms. These microorganisms incorporate this nitrogen into their cells during normal metabolic processes. After death of these microorganisms, nitrogen is returned to the nitrogen pool by mineralization of the dead cells which is a process similar to the mineralization of organic matter.

Some of the nitrogen present in the soil may be fixed permanently on clay particles. This nitrogen cannot be released from the soils. Some of the ammonium ions are fixed in the clay lattice on the cation-exchange sites by this irreversible process. Part of the nitrogen in the soil is fixed on the clay particle physically and is adsorbed on the surface alone. This temporarily fixed nitrogen on the clay particles can be utilized by the plants as well as by microorganisms present in the soil. Loss of nitrogen from soils also occurs through volatilization. If aeration of the soil is poor, certain bacteria are capable of using nitrate or nitrite nitrogen as a source of osygen. In this process nitrates and nitrites are reduced to nitrous oxides ($N_2O$ and perhaps $NO$ or $NO_2$), or to nitrogen gas ($N_2$). These products are lost to the atmosphere; this process is called denitrification. Microbial reduction of nitrites and nitrates is brought about by a number of facultative anaerobic bacteria including the genera _Psedomonas_, _Aerobacter_, _Bacillus_, etc. Under optimum conditions, nitrate reduction proceeds comparatively rapidly. The total time required for complete reduction of 300 ppm of nitrate nitrogen to nitrogen gas is only 28 to 96 hours when the temperature is held at 30°C. It is possible that nitrification and denitrification can occur in the soil at the same time. In the soil, macropores may be well aerated, while the centers of large aggregates or pockets of organic matter are deficient of oxygen. Diffusion of oxygen into these centers is often not rapid enough to replace the oxygen that is being consumed by the microorganisms.

From the foregoing discussion, it is apparent that the fate of nitrogen in the soil cannot be accurately determined. Only generalizations can be made regarding the magnitudes of the various disposition pathways of the applied nitrogen. It is assumed that 30 to 35% of the applied nitrogen is utilized by the plants. About 30% is reduced to the nitrogen oxides or nitrogen gas by the denitrification process in the anaerobic zones of the soil. The remainder of the nitrogen flows into the water bodies either through run-off or through leaching. These general values of various pathways of disposition of applied nitrogen can be considered approximate; as these values depend upon a number of environmental factors of the soil which are not completely identifiable.

## D. Disposition of Agricultural Drainage

Water applied to the agricultural land either through the natural processes of precipitation, or through an artificial irrigation system is disposed of by one of the following methods: (1) Surface Run-off; (2) Ground Water Run-off (Interflow); (3) Deep Percolation; and, (4) Evaporation and Transpiration.

Surface run-off, ground water run-off, and percolation contribute to eutrophication by providing pathways for the nutrients' movement to the lakes and streams.

Whenever precipitation occurs more rapidly than it can be absorbed by the soil, it runs off into depressions and then to rivers and lakes. Storm characteristics, soil properties, extent and kind of vegetation in the drainage basin, slope of ground, etc. influence the amount of run-off from any storm.

Water that is not lost from soil as a result of surface run-off may infiltrate and percolate into the ground and may reappear as ground water seepage, or it may percolate to deeper underground aquifers. Many factors like porosity, characteristics of the surface, vegetation, initial water content, etc. affect the infiltration rate. Components of nitrogen especially nitrates flow towards the water bodies by leaching as well as surface run-off. When nutrients percolate to the ground water, their subsequent movement to lakes or streams involve the general movement of the ground water. Nutrient content of invading water is different from the nutrient content of the ground water. Biggar and Corey write that it is not safe to assume that the nutrients derived from percolating waters will be diluted by the entire ground water.

Some of the water percolating to the ground is intercepted by the plant roots and is lost to the plant and then to the atmosphere by evapo-transpiration. Some water within the top layers of the soil comes to the surface because of capillary action and is lost also by evaporation. In this process, some salts return to the surface of the soil because of capillarity.

Recently, a controversy over fertilizer run-off with definite reference to nitrates has "boiled-over." Illinois used 10% of the total consumption of the three primary plant nutrients in the 1970 and 1971 fertilizer year, i.e.

647,972 tons of nitrogen as N, 478,497 tons of phosphate as $P_2O_5$, and 473,469 tons of potassium as $K_2O$. One observer states that the median nitrate nitrogen in Lake Decatur for 1956 to 1961 was 2.0 ppm but rose from 1966 to 1969 to 7.4 ppm. The Public Health Service lists 10 ppm of nitrate nitrogen in drinking water as a maximum acceptable standard. Illinois has proposed stringent regulations on farm fertilizer usage.

## E. Movement of Nitrogen in Soils

Loss of nitrogen nutrients by leaching has always been considered a major pathway of fertilization of lakes and streams. Soils are composed of macropores and micro-pores. Through the channels made up of these pores, water moves. Whenever the water containing nutrients moves through these channels, mixing of the soil solution and invading water takes place. Due to the presence of salts in the soils, the percolating water may have different concentrations of nutrients at various depths due to the interaction of invading solution and the solid matrix of the soil. Ions such as ammonium or phosphate may undergo exchange or adsorption. Anions like nitrates and chloride may not be adsorbed on the soil particles at all or may be adsorbed very slightly. The amount of nitrogen lost from the soils depends upon the amount of percolating water, types of soils, and other environmental factors in the soil.

Very little is known about the nutrient content of the run-off water. Sawyer on the basis of analysis of one stream tributary to each lake estimated the removal rates of nitrogen 4.4 to 6.4 pounds per acre per year for inorganic nitrogen and 1.6 to 1.8 pounds per acre per year for organic nitrogen. Values obtained are shown in tables in the original thesis. Beggar and Correy write that under conditions favorable to erosion, more nitrogen may be lost by erosion than by leaching. Organic matter has a low density relative to soil and, therefore, is more subject to movement by water action. Weibel et al conducted a number of experiments to find the values of nutrients removal in rainfall and run-off. The values average 313 pounds of suspended solids, 9 pounds of nitrogen and 0.6 pounds of phosphate as hydrolyzable phosphorus for 1.45 acre test plot.

Biggar and Correy summarize nitrogen losses for a variety of conditions. Between 4 and 50 pounds per acre per year were due to surface run-off and percolation. A major potential solution appears a retardation of the flow of nitrogen nutrients to water bodies by minimizing surface run-off as well as percolation. This is possible by improved agricultural practices and by the use of more humus and organic matter in the soil. Use of humus will increase the water holding capacity of the soil. Digested sewage sludge either in dried form or as a wet sludge is a good possibility to increase the humus matter in the agricultural soils. The use of sewage sludges in agricultural land can alleviate the solids waste problem from sewage sludges, and help to retard the flow of nitrogen from agricultural land. Experiments were performed in this investigation to study the effect of sewage sludge on flow of nitrogen from the soils. Results of these experiments are shown in the following sections.

## F. Sewage Sludges as Fertilizers

Sewage sludges have been used as fertilizers and soil conditioners for many years in various parts of the world. In the United States, the use of sewage sludge as a fertilizer has been only on golf courses, household gardening, and very small farms. Its use in large agricultural activities has not been favored by farmers because of economics and because the value of sludge as a fertilizer is limited. The sludges are low in nitrogen, phosphoric acid, and potash content. The organic matter present in sludges makes them good soil conditioners.

Chemical analyses have been made of dried sludges by many investigators. Fair and Guyer gave the following approximate fertilizer values for sewage sludges: (1) Sludge from plain sedimentation, 0.8 to 5.0% nitrogen; (2) Activated sludge, 3.0 to 10.0% nitrogen; and, (3) Trickling filter humus, 1.5 to 5.0% nitrogen. Digestion will reduce the nitrogen content by 40 to 50%. Raw sludge may contain from 1.0 to 3.0% $P_2O_5$ and 0.1 to 0.3% potash. Goldstein states that each ton of 10% solids slurry obtained from digestors usually contains 48 pounds of nitrogen, 62 pounds of phosphate, and 8 pounds of potassium.

Various methods of sludge disposal are used in wastewater management. Land disposal of sewage sludges can be considered a "natural" process when compared to any other method of sludge disposal. Sewage sludges should be considered as resource materials rather than as liabilities. Land disposal of digested sludge means planned application of this sludge to farm land for agricultural benefits. Sewage sludge contains 2 to 5% solids. Water in this sludge also contains nutrients and, therefore, is beneficial for the crops. It is noted by Evans that sewage sludges contain 16 of the 20 elements required by plants.

Although sludges have most of the elements present, yet they are very poor fertilizers because of low nitrogen and phosphorus content. It is also possible that heavy applications may produce toxic effects on plants due to presence of copper, boron and zinc, etc. from sludges of industrial wastewater treatment plants. If more organic matter is present in soils, then this will serve as toxic metal buffers. Organic matter complexes with the metal ions and may keep the soil in the homeostatic state. Schatz states that organic matter acts as a detoxification; he also writes that it is possible to apply sludges on agricultural land. When sludge applications on land are in a reasonable quantity, no harmful effects due to toxic metals are likely to be seen on the crops.

Solid portions of sewage sludges contain organic tissues which after biological decomposition become humus. This humus is a very good soil conditioner. When added to soil, sludge humus promotes aggregation of soil particles, increases the cation exchange capacity, improves aeration and also water holding and adsorption capacity of the soil.

Sludge handling and disposal are the most difficult parts of wastewater treatment and may be very costly. Various other methods used for disposal of sludges are relatively expensive as compared to the surface spreading method. Figures collected by the Metropolitan Sanitary District of Greater Chicago indicate that the cost of disposal of digested sewage sludge by land application is \$15 per equivalent dry ton. In another study, the sludge disposal costs, including collection, were found to average \$25 per ton on land whereas the costs of disposal by other methods were from \$30 to \$42 per ton.

The factors affecting the cost of surface spreading are transport distance, mode of transport, and transport efficiency. Usual modes of transport of sludges for surface spreading are trucker tank, rail, or pipeline. It is economically feasible to pump sludges through pipelines. Wasp et al found that pipeline transportation yields significant economies in comparison to truck, railroad, and ocean tanker.

Undigested sludge disposal by land spreading in agriculture has a potential of transmitting parasitic infections to humans and animals by consumption of crops raised on these farms. More hazards are involved by consumption of raw vegetables and other crops produced on sludge treated soils. This restricts the use of sewage sludges in some agricultural areas. There are, however, many crops which can safely be raised on sewage treated soils.

Sewage sludges are poor fertilizers, but when they are used along with inorganic fertilizers, the chances of leaching of fertilizers should be considerably less due to the increased organic matter present in the soils from the sludge applications. A reason for less leaching is that the water holding capacity of the sludge treated soils is increased considerably, and this gives less surface run-off and less percolation of water. With humus present the soil is mostly aerobic, and this reduces volatilization losses from the soils. Nitrates present in the soils also are consumed by the plants at a faster rate when the soils are aerobic. Experimental results are presented in subsequent pages in which sludges and nitrogen fertilizers were used together. The effects of the humus matter on retention of fertilizers, with different percentages of humus matter are shown.

## G. Experimental Design

An investigation was made in this study to find the effect of humus matter on the retention of nitrogen fertilizers in the soil. Digested sewage sludge is a good humus matter. For the 1st and 2nd runs, digested sewage sludge was used as the humus matter; and for the 3rd run, peat moss was used as the humus matter. Ammonium sulfate was used as the nitrogen fertilizer.

Instead of soil, pure silica sand was used to avoid interference of some nutrients coming into the leachate from the soil. Digested sewage sludge was mixed in different proportions with white silica sand, and this mixture was packed into the columns. A constant weight percentage of ammonium sulfate was used in the columns as the inorganic nitrogen fertilizer. Ammonium sulfate was spread on the top of the columns and mixed with the mixture.

The water percolated through the columns to determine the leachate was applied in the form of simulated rain. This was done by pricking the plastic cup to make small holes, and by filling this pricked cup with distilled water to a constant height. Approximately 200 ml. of leachate were collected at an interval of one week. This volume of water represented about 1" of percolate, and represented varying amounts of rainfall on the different columns. The leachates collected were then analysed for $SO_4^-$, concentrations. Leachates of the 2nd Run were also analysed for $NO_3^-$ and $NH_4^+$ concentrations.

The retention of nitrogen by the humus was determined indirectly. $SO_4^-$ concentrations of leachates were found as it was assumed that nitrogen ions would behave almost in a similar manner. $NO_3^-$ and $NH_4^+$ determinations were made on the 2nd Run to study the tendency of leaching of these ions. Determinations of concentrations of these ions ($NO_3^-$ and $NH_4^+$) in the 3rd Run were not successful because the leachates were highly colored and the color of the leachate was the same as the color developed by the test reagent.

$SO_4^=$ concentration of the leachates was determined by a "Standard" turbidimetric method. For this determination a Coleman Universal Spectrophotometer was used with standard cuvettes at a wave length of 420 mu. $NO_3^-$ nitrogen and $NH_4^+$ nitrogen were determined on leachates of the 2nd Run to compare with the results determined from the $SO_4^=$ values. The "Standard" method to determine the $SO_4^=$ concentration consisted of plotting a "Standard" curve for various sulfate concentrations. This curve was plotted for various $SO_4^=$ concentrations, and was used for the concentration determinations on the leachate samples. The leachate collected was vacuum filtered through millipore filters of pore size 0.30 microns, to remove any suspended matter from the percolated water. $SO_4^=$ determinations were made on these leachates exactly in the same manner as the $SO_4^=$ determinations were made for plotting the "Standard" curve.

The procedure for determining $SO_4^=$ concentrations consisted of measuring 100 ml of sample or 100 ml of properly diluted sample into a 250 ml Erlenmeyer flask. Exactly 5.00 ml of conditioning agent (to create hydrochloric acid medium having sodium chloride) was added. This was then stirred at a constant speed by a magnetic stirrer for about 30 seconds. While this solution was stirred, approximately 5 ml of 10% barium chloride solution was added; at the same instant a timer alarm clock was also started. This mixture of solutions was stirred for exactly 60 seconds. During this stirring, barium sulfate was precipitated in the form of crystals of uniform size. This suspension was then poured into the cuvette and the turbidity of the suspension (percentage transmittance) measured on the spectrophotometer using distilled water in another cuvette to read 100% transmittance.

To measure $NO_3^-$ nitrogen and $NH_4^+$ nitrogen in the leachates of the 2nd Run, colormetric determinations were made either with the sample or properly diluted sample, using a LaMotte Comparator apparatus for determining these ions in the water. This apparatus is very commonly used in the science of hydroponics. These tests are not "Standard" tests; they give results which are sufficiently accurate to determine the trend of leaching of these ions from the columns used in the experiments.

## H. Discussion of Results

The data collected and plotted in the original thesis show that the increasing amount of humus in the soil has a strong tendency to retain the nutrients during the initial periods of leachings. As the columns are leached successively, the total percentage of nutrients (sulfates) leached in 1st and 2nd leachates of the columns is higher with the lower percentages of humus. The columns having higher percentages of humus tend to retain the nutrients for the first few times the columns are leached. However, as the columns are leached further, the percentage of nutrients leached in each leaching also increases in the columns having higher percentage of humus. This means that most of the nutrients will be eventually leached, and the total percentage of nutrients leached will be approximately the same when all the columns have been leached for a large number of times.

The results show that when sludge is used as the humus matter, the percentages of sulfate nutrient leached are higher in columns having 10% humus. The data regarding percentage of sulfate leached, when peat moss is used as humus, show successively decreasing values as the humus is increased in the mixture. The values presented in the tables and in all figures (of the original thesis) show that the sulfate nutrients are held in the columns for longer periods when humus is used. All the figures show that the rate of leaching decreases as the humus matter is increased in the columns up to about 40% of humus. Above this percentage of humus in the soil, there is not any appreciable increase in retention of nutrients in the soil as more humus is used. Another interesting finding of this study is that sulfate nutrients leached per inch length of column have successively low values as the percentage of humus increases in the columns. This shows that the amount of nutrients moved per unit length in the soil is lower when the amount of humus is higher.

It is also found that the amount of rainfall required to create 1" of percolate is more as the percentage of humus is increased. This means that the sand column requires less distilled water to get 1" of percolate (about 200 ml. of leachate) in comparison to the columns having various percentages of humus in them. Distilled water required in the column having 40% humus is almost three times the distilled water required for the column having no humus. One inch of percolate in this discussion means a sheet of water of thickness one inch when it has already passed through the soil columns. However, when the humus values in the soil-humus mixture are very high, the amount of rainfall to create 1" of percolate decreases again. This is possibly due to increased voids in the mixture with a tendency of the water to rush through the voids.

Results obtained with the peat moss as humus are comparable to those when digested sludge is used as the humus. Peat moss holds less water in it in comparison to sewage sludge. The values for percentage sulfate leached are usually higher when peat moss is used as humus instead of digested sewage sludge. Higher percentages of peat moss as humus were relatively less effective in holding the nutrients.

Nitrate and ammonia values were determined on leachates of the 2nd Run. It was tried to determine the nitrate and ammonia values of the 3rd Run, but these determinations could not be defined due to an inability to determine the correct value of the color developed. The color of the leachate was the same as the color developed in the test used. At higher concentrations it was not possible to differentiate the color of leachate from that of the test color; and at lower concentrations it was not possible to see the color developed. The 2nd Run values for the nitrates and the ammonia have shown the similar tendencies for leaching as are shown by the sulfate values. Relatively more nitrates are formed and leached, when the humus is present in the columns. More ammonia is leached in the column when there is no humus present in the column. This is due to the absence of microorganisms in the silica sand columns; for this reason ammonia is not converted to nitrates. It is not possible to conclude definitely that nitrates and ammonia nitrogen behave similarly to the sulfates in the presence of humus. However, this study shows that the tendency of leaching of sulfate and nitrogen ions is quite similar. Therefore, more humus in soils is likely to retard the movement of nitrogen to the water environment. This study has shown that this idea should be investigated intensively by more extensive laboratory study, and by field experiments.

## I. Conclusions

(a) Increasing percentage of humus in the soil increases the water holding capacity of the soil. This means that to create 1" of percolate in various percentage humus mixtures, one needs larger amounts of rainfall.

(b) The percent of the nutrients leached is higher when less humus is present in the soil.

(c) The percent of the nutrients leached in each column approaches a 100% total when the columns are leached a large number of times.

(d) Amount of nutrients moved per inch length of the mixture decreases as the percentage of humus in the soil increases.

(e) Amount of nutrients leached per inch of rainfall is successively less as the percentage of humus is increased in the mixture.

(f) 30 to 40% of humus in the mixture is the best percentage to obtain maximum results for retention of the nutrients. More than 40% of humus in the mixture does not help to retain significantly more nutrients.

## J. Recommendations For Future Work

(a) Larger scale investigations with closer values of percentages of the humus in the columns should be carried out in the laboratory. The values for sulfate, nitrate, ammonia, and total nitrogen should be determined on each leachate by "Standard" methods.

(b) Further studies should be undertaken on beds of a size at least 6' x 6' x 4' with percolates taken at various depths for an investigation of the trend of leaching.

(c) Plots of larger scale for field testing should be used so that the leaching trends in the field can be investigated using various percentages of humus to certain plots, and contiguous plots with no humus for field comparisons.

## K. References and Appendices

The reference thesis on which this chapter is based contains 24 tables; of these tables 16 contain the laboratory experimental data. There are included also 35 figures; of which 28 are plotted curves of the data experimentally determined. The appendix lists 28 pertinent references.

The complete reference thesis is available through the Solid Waste Information Retrieval System (SWIRS) or through an Inter-Library Loan from Syracuse University.